

Physical Chemistry Part 2

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Solutions

OVERVIEW

- 1. Solution:** A homogeneous mixture of two or more components whose concentration can be varied within a limit.

Alternatively, a mixture of solute and solvent is called solution.

- 2. Solubility:** The amount of solute which can be dissolved in 100 g of a solvent is called its solubility to make a saturated solution.

If the hydration energy is greater than the lattice energy, then the solute is soluble in solution and energy is released, i.e., ΔH solution is negative.

- 3. Vapour pressure of liquid:** At a given temperature, the pressure exerted by the vapours when they are in equilibrium with the liquid is called the vapour pressure of the liquid.

Greater the force of attraction between liquid molecules, lower is the vapour pressure and vice versa.

- 4. Vapour pressure of a solution:** A solution is formed when a miscible solute is added to a pure solvent. Some solute molecules replace the molecules of solvent from the surface. Therefore, the escaping tendency of the solvent molecules decreases, which causes lowering in the vapour pressure of solution, that is, $p_{\text{solution}} < p^\circ$

- 5. a. Raoult's law**

When two miscible volatile liquids are heated, the partial pressure of one component is equal to the product of the mole fraction and pure pressure of that component. Alternatively, the partial pressure of each component in the solution is directly proportional to its mole fraction.

$$\therefore P_{\text{total}} \propto \chi_A \text{ or } \chi_B$$

- b.** If only solvent component (A) is volatile, then the vapour pressure of solution is $p_s = P_A^\circ \chi_A$.
- c.** Mole fraction of solvent (A) in vapour phase,

$$\chi_A^v = \frac{p_A}{P_{\text{total}}}$$

- 6. Ideal solution:** They obey Raoult's law for all ranges of concentration and temperature. In these solutions solute-solute and solvent-solvent interactions are almost similar to solute-solvent interactions. Substances having similar structures and polarities form nearly ideal solutions, e.g., $\text{C}_2\text{H}_5\text{Br} + \text{C}_2\text{H}_5\text{I}$.

A–A or B–B interaction = A–B interaction

$$\Delta_{\text{mix}} H = 0$$

$$\Delta_{\text{mix}} V = 0$$

- 7. Non-ideal solutions**

They do not obey Raoult's law at any concentration. These are solutions in which solute-solute and solvent-solvent interactions are different than solute-solvent interactions.

A–A or B–B interaction \neq A–B interaction.

$$\Delta_{\text{mix}} H \neq 0$$

$$\Delta_{\text{mix}} V \neq 0$$

There are two types of such solutions:

- a.** Solutions which show positive deviations from ideal solution if A–A or B–B interaction $>$ A–B interaction.

$$\Delta_{\text{mix}} H > 0 \text{ and } \Delta_{\text{mix}} V > 0$$

- b.** Solutions which show negative deviation from ideal solution if A–A or B–B interaction $<$ A–B interaction.

$$\Delta_{\text{mix}} H < 0 \text{ and } \Delta_{\text{mix}} V < 0$$

- 8. Henry's law: (solubility of a gas in liquid):** At constant temperature, the solubility of a gas in a liquid is directly proportional to the pressure of the gas. The solubility of gases increases with increase of pressure and decreases with increase of temperature. Henry's law states that "the partial pressure of the gas in the vapour phase (p) is proportional to the mole fraction of the gas (χ) in the solution" and is expressed as:

$$p = K_H \chi$$

where K_H is Henry's law constant and χ is the mole fraction of solute.

- 9. Azeotropic or constant boiling mixtures:** A liquid mixture having a definite composition and boiling like a pure liquid is called a *constant boiling mixture* or an *azeotropic mixture* or simply an azeotrope. Azeotropic mixtures are of two types:

- a. Minimum boiling azeotropes:** The boiling point of an azeotrope is less than the boiling point of either of the pure components.

- b. Maximum boiling azeotropes:** The boiling point of an azeotrope is higher than that of either of the pure components.

Azeotropic mixtures cannot be separated into their constituents by fractional distillation.

- 10. Colligative properties:** Certain properties of ideal solutions depend only on the number of particles of the solute in a definite amount of the solvent and do not depend on the nature of solute. Such properties are called colligative properties.

11. Relative lowering of vapour pressure

$$\frac{P^\circ - P_s}{P^\circ} = \chi_B = \frac{n_B}{n_A + n_B}$$

where P° = Vapour pressure of pure solvent

P_s = Vapour pressure of solution

χ_B = Mole fraction of solute

n_A, n_B = Moles of solvent and solute

In terms of molecular weight of solute

$$Mw_B = \frac{W_B \times Mw_A}{W_A \left(\frac{P_A^\circ - P_s}{P^\circ} \right)}$$

$$\frac{P^\circ - P_s}{P_s} = \frac{n_B}{n_A} \quad (\text{for all kinds of solutions})$$

$$\frac{P^\circ - P_s}{P^\circ} = \frac{n_B}{n_A} \quad (\text{for dilute solutions})$$

- 12. Osmosis:** The net spontaneous flow of the solvent molecule from the solvent to the solution or from a less concentrated solution to a more concentrated solution through a semi-permeable membrane is called osmosis.

$$\text{Osmotic pressure } (\pi) = CRT = \frac{n}{V} RT$$

In term of molecular weight

$$\pi = \frac{W_B RT}{V Mw_B} \quad \text{or} \quad Mw_B = \frac{W_B RT}{V \pi}$$

- 13. Isotonic solutions:** Solutions having same osmotic pressure are called isotonic or isosmotic solutions. A pure solution of 0.91% NaCl is isotonic with human red blood cells (RBCs). Therefore, in this solution RBCs neither swell nor undergo plasmolysis. The shrinking of cell due to the flow of water out of the cell is called *plasmolysis* or *crenation*.

- 14. Hypertonic solutions:** The solution which has higher osmotic pressure than any other solution is called hypertonic solution.

A pure NaCl solution with concentration more than 0.91% is called hypertonic solution. On placing RBCs in this solution, they shrink due to plasmolysis.

- 15. Hypotonic solutions:** The solution which has lower osmotic pressure than some other solution is called hypotonic solution. A pure NaCl solution with concentration less than 0.91% is called *hypotonic solution*. On placing RBCs in this solution, they will swell and even burst. The process of swelling of the cell resulting into rupturing of the cell is known as *hemolysis*.

16. Elevation in boiling point (ΔT_b)

$$\Delta T_b = K_b m; \quad K_b = \text{molal elevation constant}$$

$$m = \text{molality}$$

$$= \frac{K_b \times 1000 \times W_B}{W_A \times Mw_B}$$

$$\therefore K_b = \frac{Mw_A RT_b^2}{\Delta_{\text{vap}} H \times 1000} \quad \text{or} \quad \frac{RT_b^2}{l_v \times 1000}$$

$\Delta_{\text{vap}} H$ = Enthalpy of vapourization

$$l_v = \text{Latent heat of vapourization} = \left(\frac{\Delta_{\text{vap}} H}{Mw_{\text{solvent}}} \right)$$

Molal elevation constant (K_b) may be defined as the elevation in boiling point when the molality of the solution is unity.

Unit of K_b is K m^{-1} or $^\circ\text{C m}^{-1}$ or K kg mol^{-1} .

17. Depression in freezing point (ΔT_f)

$\Delta T_f = T_0 - T_s = K_f \times m$; where K_f is molal depression constant or cryoscopic constant.

$$\text{or } \Delta T_f = \frac{K_f \times 1000 \times W_B}{W_A \times Mw_B}$$

$$= \frac{Mw_A \times RT_f^2}{\Delta_{\text{fus}} H \times 1000} \quad \text{or} \quad \frac{RT_f^2}{l_f \times 1000}$$

$$\left(l_f = \text{latent heat of fusion} = \frac{\Delta_{\text{fus}} H}{Mw_{\text{solvent}}} \right)$$

Unit of K_f is K m^{-1} or $^\circ\text{C m}^{-1}$ or K kg mol^{-1} .

- 18. Molecular masses of macromolecules (i.e., polymers and proteins)** are determined by osmotic pressure method because other colligative properties give so low values which are difficult to measure. Moreover, these methods require heating which changes their properties (e.g., proteins are coagulated on heating).

- 19. All colligative properties** $\left(\text{e.g., } \frac{\Delta P}{P^\circ}, \Delta T_b, \Delta T_f, \text{ and } \pi \right)$ are directly proportional to the number of moles of solutes. But freezing point and vapour pressure of the solution
- $$\propto \frac{1}{\text{Number of moles of solutes}}.$$

20. Relationship between different colligative properties

- a. Osmotic pressure (π) with relative lowering of vapour pressure:**

$$\pi = \frac{P^\circ - P_s}{P^\circ} \times \frac{dRT}{Mw_B}$$

$$\left[\begin{array}{l} d = \text{density of the solution} \\ Mw_B = \text{Molecular mass of solute} \end{array} \right]$$

- b. Osmotic pressure (π) with depression in boiling point (ΔT_b):**

$$\pi = \Delta T_b \times \frac{dRT}{1000 K_b}$$

- c. Osmotic pressure (π) with depression in freezing point (ΔT_f):

$$\pi = \Delta T_f \times \frac{dRT}{1000K_f}$$

- d. Elevation in boiling point with relative lowering of vapour pressure:

$$\Delta T_b = \frac{1000 K_b}{Mw_A} \left(\frac{P^\circ - P_s}{P^\circ} \right) \quad \left[Mw_A = \text{Molecular mass of solvent} \right]$$

- e. Depression in freezing point with relative lowering of vapour pressure:

$$\Delta T_f = \frac{1000 K_f}{Mw_A} \left(\frac{P^\circ - P_s}{P^\circ} \right)$$

21. Van't Hoff factor (i)

$$i = \frac{\text{Observed colligative property}}{\text{Normal colligative property}}$$

$$= \frac{\text{Normal (calculated) molecular mass}}{\text{Abnormal (observed) molecular mass}} = \frac{Mw_{(c)}}{Mw_{(o)}}$$

For substances undergoing association or dissociation in the solution, the various expressions for the colligative properties are modified as follows:

$$\Delta T_b = iK_b m$$

$$\Delta T_f = iK_f m$$

$$\frac{\Delta P}{P^\circ} = i\chi_{\text{solute}}$$

$$\pi = iCRT$$

22. van't Hoff factor, $i > 1$, if there is dissociation of the solute in the solution and $i < 1$ if there is association of the solute in the solution.

For 100% dissociation of a solute, i = number of ions produced from one molecule of the solute.

\Rightarrow If observed colligative property < calculated value or $Mw_{(o)} < Mw_{(c)}$ (or $i < 1$), there is association.

\Rightarrow If observed colligative property > calculated value or $Mw_{(o)} < Mw_{(c)}$ (or $i > 1$), there is dissociation.

2.1 INTRODUCTION

A solution is a homogeneous mixture of two or more than two components dispersed on a molecular scale. A solution depending upon the number of components can be classified as binary solution (two components), ternary solution (three components), quaternary solution (four components), and so on. In solution the component which is present in excess amount is called the solvent and the component which is present in lesser amount is called as solute. In other words a solute is a substance that dissolves while solvent is a substance in which dissolution takes place. A solution is a single-phase system and the components may be in solid, liquid, or gaseous state, and therefore, different types of solutions are possible and summarized in Table 2.1.

Table 2.1 Different types of solutions

Type of solutions	Common example
<i>Gaseous solution</i>	
Gas in gas	A mixture of oxygen and nitrogen gases
Liquid in gas	Chloroform vapours mixed with nitrogen gas
Solid in gas	Camphor vapours in nitrogen gas
<i>Liquid solution</i>	
Gas in liquid	Oxygen dissolved in water
Liquid in liquid	Ethanol dissolved in water
Solid in liquid	Sucrose dissolved in water
<i>Solid solution</i>	
Gas in solid	Solution of hydrogen in palladium
Liquid in solid	Amalgam of mercury with sodium
Solid in solid	Copper dissolved in gold

2.2 TYPES OF SOLUTION

2.2.1 SOLID SOLUTION

Solid in Solid

This type of solution is formed by mixing two solid components. For example, brass bronze, monel metal, and steel.

Solid solutions are classified into two categories: substitutional solid solutions and interstitial solid solutions.

- (a) Substitutional solid solutions are formed by placing atoms of one kind into the place of other substance in its crystal lattice as shown in Fig. 2.1. Brass is a common example of the substitutional solid solution of copper and zinc.

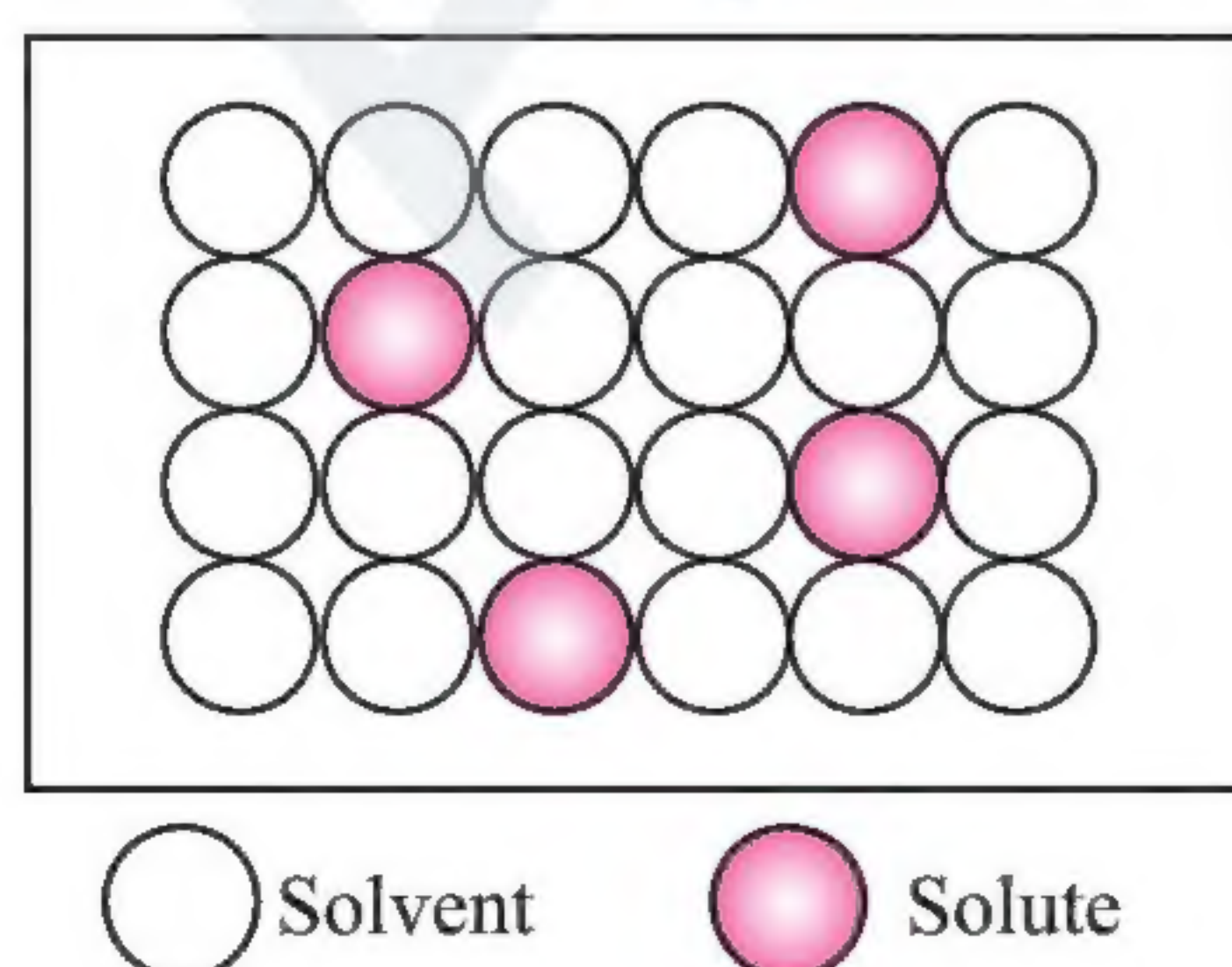


Fig. 2.1 Substitution solid solution

- (b) Interstitial solid solutions are formed by placing atoms of one kind into the voids in the lattice of atoms of other substance as shown in Fig. 2.2. Tungsten carbide, an extremely hard substance, is a common example of interstitial solid solutions.

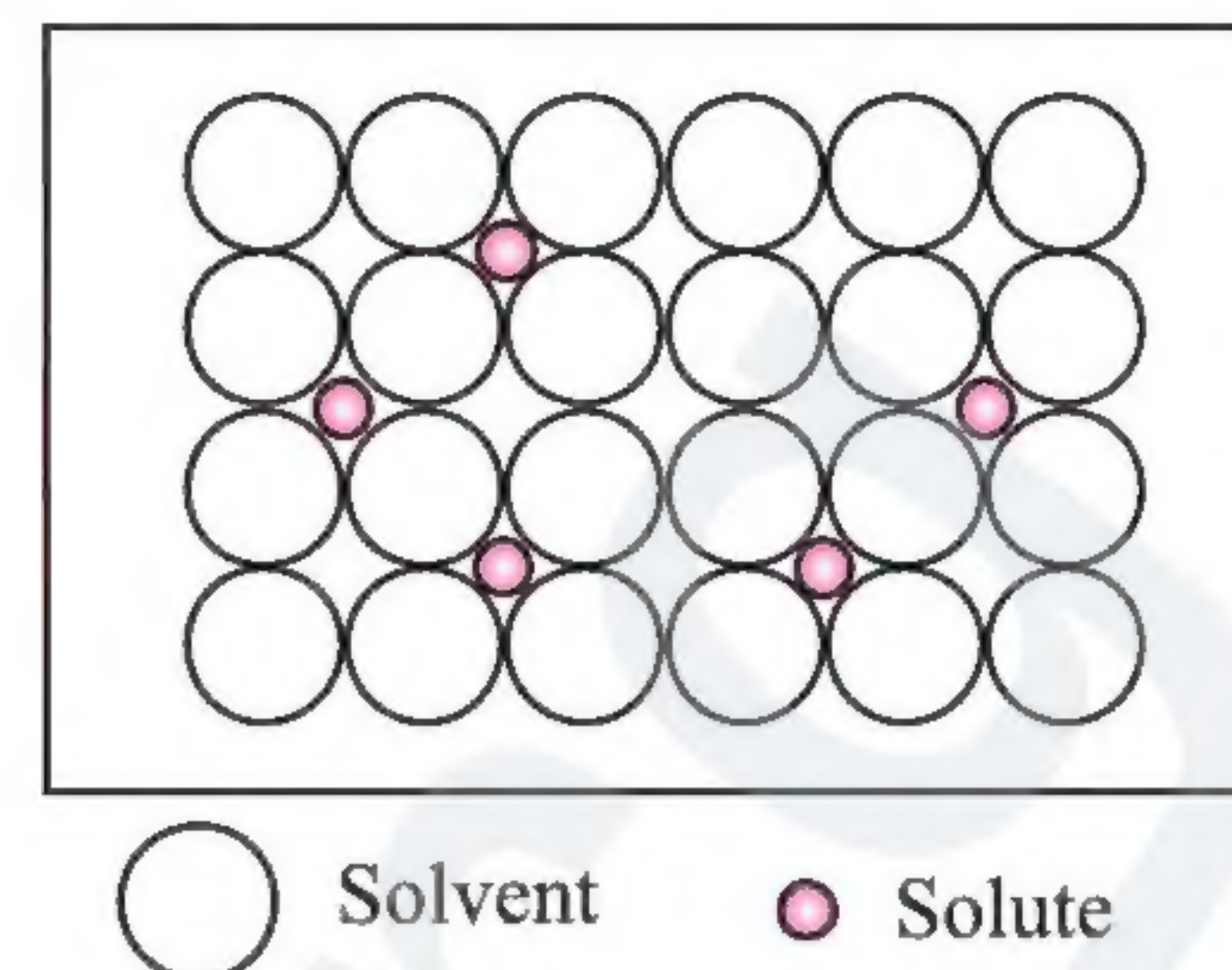


Fig. 2.2 Interstitial solid solution

Solutions of Solids in Liquid

The solubility of a solid in a liquid at any temperature is defined as the maximum amount of the solid (solute) in grams which can dissolve in 100 g of the liquid (solvent) to form a saturated solution at that particular temperature.

Following are the factors affecting the solubility of a solid in a liquid.

- (a) *Nature of the solute and solvent*

In general, a solid dissolves in a liquid which is chemically similar to it. It can be also said as “like dissolves like”, i.e., an ionic compound or polar compound dissolves in a polar solvents whereas non-polar compounds dissolve in non-polar solvents.

For example, common salt (an ionic compound) is more soluble in water (a polar solvent). Similarly, non-polar (i.e., covalent or organic) iodine is more soluble in alcohol or carbon tetrachloride (covalent liquids).

The reason for the solubility of an ionic compound in polar solvent is because of strong electrostatic forces of attraction between the ions of the crystal and the polar solvent molecules, the negative ions being attracted by the positive poles of the solvent molecules and the positive ions by the negative poles of the solvent molecules. For example when water is used as the solvent (Fig. 2.3), the water molecules pull the ions of the crystal apart and the electrostatic forces of attraction existing between the ions are surrounded by the water molecules which act as an envelope around the ions and prevent the recombination of ions. The ions thus moving freely in the solution are said to be *hydrated*. It may be mentioned here that whereas energy is required for the splitting of the ionic compound into ions (called *lattice energy*), energy is given out when the ions get *hydrated* (called *hydration energy*). A substance dissolves if there is not evolution of energy, i.e., lowering of energy occurs which will happen if hydration energy is greater than the lattice energy.

The other polar solvents are liquid ammonia, liquid hydrogen sulphide, and liquid sulphur dioxide which are also good solvents for ionic compounds.

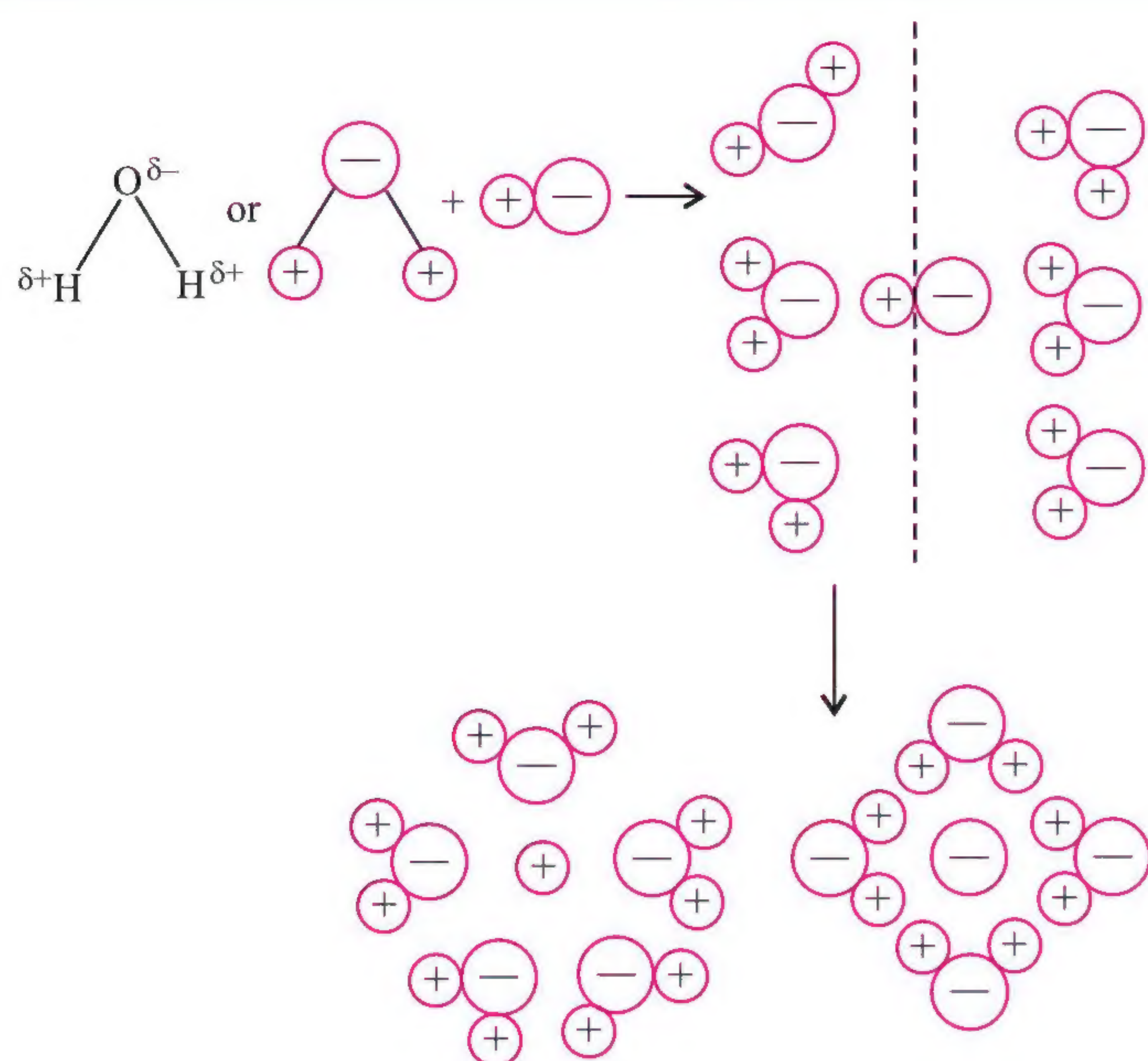


Fig. 2.3 Dissolution of an ionic compound in a polar solvent water (H_2O)

The solubility of non-polar compounds is due to similar solute–solute, solute–solvent, and solvent–solvent interactions.

(b) Effect of temperature on solubility: Solubility curve

Various ionic substances can be classified into three categories based on the effect of temperature on solubility in water.

(i) Ionic substances whose solubility decreases continuously with increase of temperature

There are a few substances such as cerium sulphate, lithium carbonate, sodium carbonate monohydrate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$), etc., whose solubility decreases with increase of temperature.

(ii) Ionic substances whose solubility increases continuously with increase of temperature

Most of the substances such as NaNO_3 , KNO_3 , NaCl , KCl , etc., fall in this category. The reason for this behaviour is that in case of all such substances, the process of dissolution is endothermic, i.e.,



on applying Le Chatelier's principle, as the temperature is increased, equilibrium will shift in a direction in which the heat is absorbed, i.e., in the forward direction. Consequently, more of the solute passes into the solution.

(iii) Ionic substance whose solubility does not increase or decrease continuously.

There are some substances which on heating change at a particular temperature from one polymorphic form to another (like α to β form as in the case of ammonium nitrate) or from one hydrated form to another (e.g., $\text{CaCl}_2 \cdot 6\text{H}_2\text{O} \longrightarrow \text{CaCl}_2 \cdot 4\text{H}_2\text{O} \longrightarrow \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) or from hydrated to anhydrous form (e.g., $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \longrightarrow \text{Na}_2\text{SO}_4$). The temperature at which one form of the substance changes into another is called *transition temperature*.

Such substances do not show a continuous increase or decrease of solubility. For example, the solubility of

sodium sulphate first increases upto 32.4°C and then begins to decrease.

When solubilities are plotted against temperatures, the curve obtained is called *solubility curve*.

2.2.2 GASEOUS SOLUTION

All the gases form a homogeneous mixture and are therefore regarded as solutions. Air is an example of gaseous solutions; more examples are listed in Table 2.1.

2.2.3 LIQUID SOLUTION

Liquid solutions are formed by mixing solids or gases in liquid or liquid in liquid homogeneously. Examples of liquid solutions are listed in Table 2.1.

2.3 METHODS OF EXPRESSING THE CONCENTRATION OF A SOLUTION AND “n” FACTOR

Refer to overview point (1-14) chapter 1 and overview point (1-30) chapter 3, physical chemistry part 1.

2.4 SOLUBILITY OF A GAS IN A LIQUID

Gases dissolve in liquids to form homogeneous solutions. For example, soda water contains carbon dioxide dissolved in water under high pressure. Oxygen is sufficiently soluble in water to allow the survival of aquatic life in lakes, rivers and oceans.

The solubility of a gas in a liquid (also called the solubility co-efficient) can be defined as the volume of the gas (in cm^3) which will dissolve in 1 cm^3 of the liquid to form a saturated solution at particular temperature and pressure.

The solubility of a gas in a liquid is determined by several factors:

(a) The nature of the gas and the solvent: The solubility of different gases varies considerably in the same solvent. Some gases are more soluble whereas some gases are less soluble, i.e., it depends upon the nature of gas, e.g., oxygen, nitrogen, helium, and argon are less soluble in water whereas sulphur dioxide, hydrogen chloride, and ammonia are more soluble in water because they chemically react with water and form sulphurous acid, hydrochloric acid, and ammonium hydroxide, respectively.

(b) The effect of temperature: The solubility of a gas decreases with increase in temperature. This is because on heating the solution of a gas some gas is usually expelled out of the solution. This can be understood as follows:

The dissolution of a gas in an exothermic process, i.e., it is accompanied by evolution of heat



On applying Le Chatelier's principle, it is evident that the increase in temperature would shift the equilibrium in the backward direction, i.e., the solubility would decrease.

Though generally the solubility of a gas in a liquid decreases with increase in temperature, there are some exceptions. For example, the solubility of some sparingly soluble gases, such

as hydrogen and inert gases, increases slightly with increase of temperature, specially in the non-aqueous solvent such as hydrocarbons, alcohol, and acetone.

- (c) Effect of pressure: The solubility of gases increases with increase of pressure.

Henry's law gives a quantitative relationship between the solubility of gas and the pressure. This law states that at a given temperature the mass of dissolved gas in a given volume of solvent is proportional to the pressure of the gas with which it is in equilibrium.

If m is the mass of the gas dissolved by unit volume of the solvent, and the pressure of the gas at equilibrium with solution is P , then according to Henry's law,

$$m \propto P \text{ or } m = K \cdot P$$

where K is the proportionality constant and depends upon the nature of gas, nature of solvent, temperature, and units of pressure.

If we plot a graph between the solubility of gas and the equilibrium pressure at a constant temperature, a straight line would be observed (Fig. 2.4).

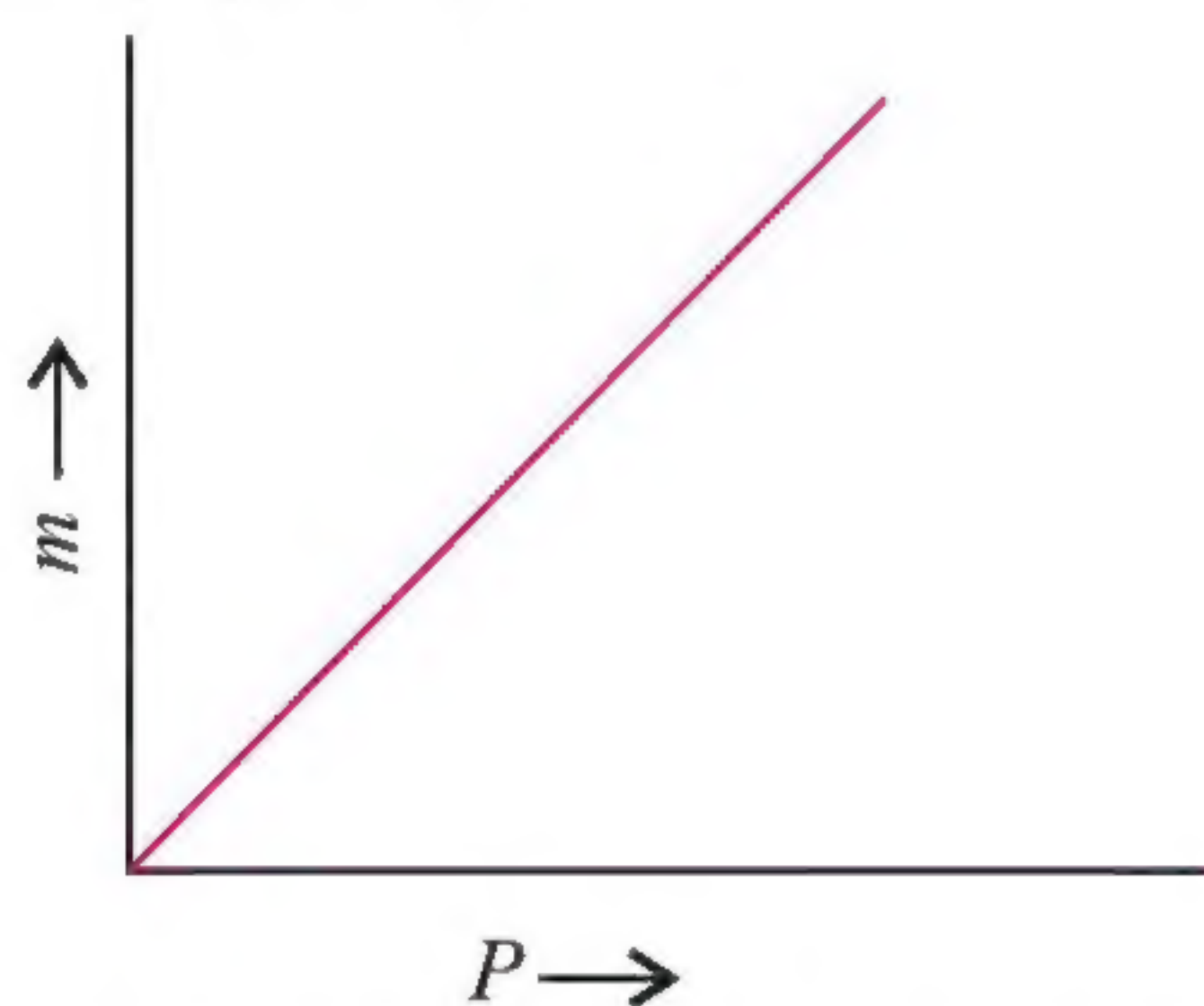


Fig. 2.4 Variation of solubility of gas with pressure

Figure 2.5 shows the variation of solubility of some gases at equilibrium pressure over the solution.

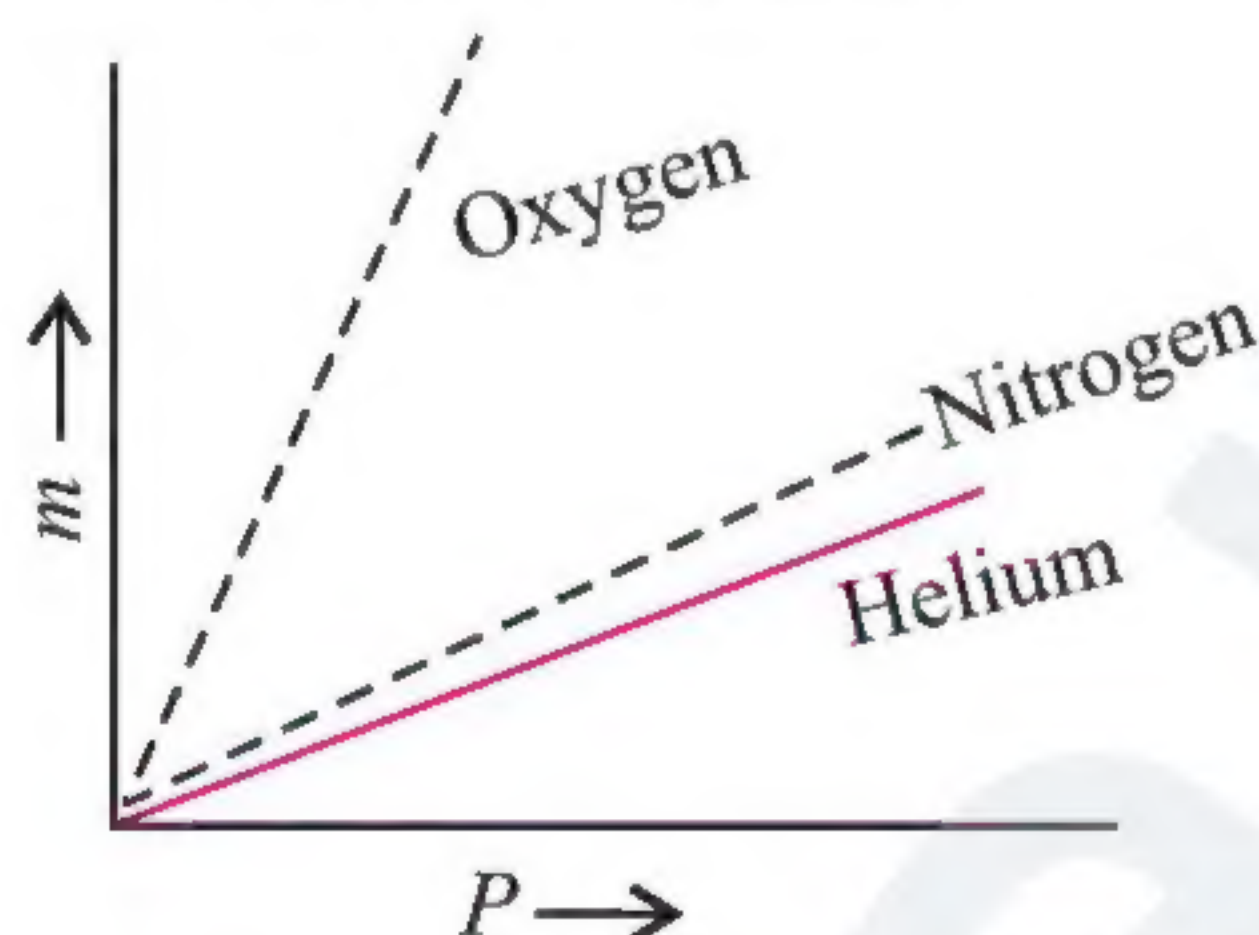


Fig. 2.5 Variation of solubility of some gases with equilibrium pressure

The variation of these gases depends upon their nature. Dalton, a contemporary of Henry, concluded independently that the solubility of a gas in a liquid solution depends upon the partial pressure of the gas.

2.4.1 HENRY'S LAW IN THE FORM OF MOLE FRACTION

According to Henry's law, the mass of gas (W_2) dissolved in a given volume of solvent of mass (W_1) at equilibrium pressure is given as

$$W_2 = KP \quad \dots(i)$$

Divide Eq. (i) by W_1 , the mass of solvent, we have

$$\frac{W_2}{W_1} = \frac{K}{W_1} P = K'P \quad \left(\frac{K}{W_1} = K' \right) \quad \dots(ii)$$

Divide the two masses by their respective molar masses, we have

$$\frac{W_2/M_{w_2}}{W_1/M_{w_1}} = \left(\frac{K' M_{w_1}}{M_{w_2}} \right) P = K''P \quad \dots(iii)$$

$$\text{or } \frac{n_2}{n_1} = K''P \quad \left(\text{moles } (n) = \frac{W}{M_w} \right) \quad \dots(iv)$$

The amount fraction of the gas in the solution is given as

$$\chi_2 = \frac{n_2}{n_1 + n_2} \quad \dots(v)$$

If the solution is very dilute, i.e., $n_2 \ll 1$, Eq. (v) can be written as

$$\chi_2 = \frac{n_2}{n_1} \quad \dots(vi)$$

Now substituting this equation in Eq. (iv), we get

$$\chi_2 = K''P$$

$$\text{or } P = \frac{1}{K''} \chi_2$$

$$P = K_H \chi_2 \quad \left(K_H = \frac{1}{K''} \right) \quad \dots(vii)$$

where K_H is called Henry's law constant. Thus, Henry's law can also be stated as: the pressure of a gas over a solution in which the gas is dissolved is equal to the amount fraction of the dissolved gas multiplied by Henry's constant.

Different gases have different K_H values at the same temperature. This suggests that K_H is a function of the nature of the gas.

It is obvious from Eq. (vii) that the higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid. K_H value for both N_2 and O_2 increases with increase of temperature indicating that the solubility of gases decreases with increase of temperature. It is due to this reason that aquatic species are more comfortable in cold waters rather than in warm waters.

ILLUSTRATION 2.1

If N_2 gas is bubbled through water at 293 K, how many millimoles of N_2 gas would dissolve in 1 L of water. Assume that N_2 exerts a partial pressure of 0.987 bar. Given that Henry's law constant for N_2 at 293 K is 76.48 kbar.

Sol. The solubility of gas is related to its mole fraction in the aqueous solution. The mole fraction of the gas in the solution is calculated by applying Henry's law. Thus,

$$\chi_{N_2} = \frac{p_{N_2}}{K_H} = \frac{0.987 \text{ bar}}{76480 \text{ bar}} = 1.29 \times 10^{-5}$$

As 1 L water contains 55.5 mol of it, therefore, if n represents number of moles of N_2 in solution, then

$$\chi_{N_2} = \frac{n \text{ mol}}{n \text{ mol} + 55.5 \text{ mol}} \approx \frac{n}{55.5} = 1.29 \times 10^{-5}$$

$$\text{Thus, } n = 1.29 \times 10^{-5} \times 55.5 \text{ mol}$$

$$= 7.16 \times 10^{-4} \text{ mol}$$

$$= 7.16 \times 10^{-4} \text{ mol} \times \frac{1000 \text{ mmol}}{1 \text{ mol}}$$

$$= 0.716 \text{ mmol}$$

ILLUSTRATION 2.2

Henry's law constant for oxygen dissolved in water is 4.34×10^4 atm at 25°C . If the partial pressure of oxygen in air is 0.4 atm. Calculate the concentration (in moles per litre) of the dissolved oxygen in water in equilibrium with air at 25°C .

Sol.

Given:

Henry's law constant, $K_H = 4.34 \times 10^4$ atm $p_{\text{O}_2} = 0.4$ atm

According to Henry's law,

$$p = K_H \chi$$

$$\therefore p_{\text{O}_2} = K_H \chi_{\text{O}_2}$$

$$\text{or } \chi_{\text{O}_2} = \frac{p_{\text{O}_2}}{K_H} = \frac{0.4}{4.34 \times 10^4} = 9.2 \times 10^{-6}$$

$$\text{Moles of water } (n_{\text{H}_2\text{O}}) = \frac{1000}{18} = 55.5 \text{ mol}$$

$$\text{Mole fraction of oxygen } (\chi_{\text{O}_2}) = \frac{n_{\text{O}_2}}{n_{\text{O}_2} + n_{\text{H}_2\text{O}}}$$

Since n_{O_2} is very small in comparison to $n_{\text{H}_2\text{O}}$,

$$\therefore \chi_{\text{O}_2} = \frac{n_{\text{O}_2}}{n_{\text{H}_2\text{O}}}$$

$$\text{or } \chi_{\text{O}_2} \times n_{\text{H}_2\text{O}} = n_{\text{O}_2}$$

$$9.2 \times 10^{-6} \times 55.5 = n_{\text{O}_2}$$

$$\text{or } n_{\text{O}_2} = 5.11 \times 10^{-4} \text{ mol}$$

Since 5.11×10^{-4} mol are present in 1000 mL of solution, therefore, molarity = 5.11×10^{-4} M.

ILLUSTRATION 2.3

Henry's law constant for the solubility of N_2 gas in water at 298 K is 1.0×10^5 atm. The mole fraction of N_2 in air is 0.6. The number of moles of N_2 from air dissolved in 10 moles of water at 298 K and 5 atm pressure is

a. 3.0×10^{-4}

b. 4.0×10^{-5}

c. 5.0×10^{-4}

d. 6.0×10^{-6}

Sol.

$$\begin{aligned} \text{a. Partial pressure of } \text{N}_2 \text{ in air } (p_{\text{N}_2}) &= P_{\text{total}} \times \chi_{\text{N}_2}(\text{in air}) \\ &= 5 \times 0.6 \end{aligned}$$

$$p_{\text{N}_2}(\text{in air}) = K_H \times \chi_{\text{N}_2}(\text{in H}_2\text{O})$$

$$5 \times 0.6 = 1.0 \times 10^5 \times \chi_{\text{N}_2}(\text{in H}_2\text{O})$$

$$\chi_{\text{N}_2} \text{ in 10 moles of water} = \frac{5 \times 0.6}{1.0 \times 10^5} = 3.0 \times 10^{-5}$$

$$\chi_{\text{N}_2} = \frac{n_{\text{N}_2}}{n_{\text{N}_2} + n_{\text{H}_2\text{O}}}$$

$$3.0 \times 10^{-5} = \frac{n_{\text{N}_2}}{n_{\text{N}_2} + 10}$$

$$\begin{aligned} n_{\text{N}_2} \times 3 \times 10^{-5} + 3 \times 10^{-5} \times 10 &= n_{\text{N}_2} \\ 3 \times 10^{-4} &= n_{\text{N}_2} (1 - 3 \times 10^{-5}) \quad [1 - 3 \times 10^{-5} \approx 1] \end{aligned}$$

$$\therefore n_{\text{N}_2} = 3 \times 10^{-4}$$

ILLUSTRATION 2.4

At same temperature, oxygen is more soluble in water than hydrogen. Which of them will have a higher value of K_H and why?

Sol. Hydrogen will have higher value of K_H because if gas has higher solubility, its K_H value is lower.

ILLUSTRATION 2.5

For a solution of acetone in chloroform, Henry's law constant is 150 torr at a temperature of 300 K. (a) Calculate the vapour pressure of acetone when the mole fraction is 0.12. (b) Assuming that Henry's law is applicable over sufficient range of composition to make the calculation valid, calculate the composition at which Henry's law pressure of chloroform is equal to Henry's law pressure of acetone at 300 K. (Henry's law constant for chloroform is 175 torr.)

Sol.

a. The given values are

$$K_H = 150 \text{ torr}; \chi_{\text{acetone}} = 0.12$$

Using Henry's law equation

$$P = K_H \chi, \text{ on substituting all values}$$

$$P = (150 \text{ torr}) (0.12) = 18.0 \text{ torr}$$

b. Here $P = 18.0$ torr, and $K_H = 175.0$ torr

$$\therefore \chi_{\text{acetone}} = \frac{P}{K_H} = \frac{18.0 \text{ torr}}{175.0 \text{ torr}} = 0.103$$

ILLUSTRATION 2.6

Henry's law constant for oxygen and nitrogen dissolved in water at 298 K are 2.0×10^9 Pa and 5.0×10^9 Pa, respectively. A sample of water at a temperature just above 273 K was equilibrated with air (20% oxygen and 80% nitrogen) at 1 atm. The dissolved gas was separated from a sample of this water and then dried. Determine the composition of this gas.

Sol. The given values are:

$$K_{\text{H}(\text{O}_2)} = 2 \times 10^9 \text{ Pa}; K_{\text{H}(\text{N}_2)} = 5 \times 10^9 \text{ Pa}$$

Partial pressure of oxygen,

$$p_{\text{O}_2} = 0.2 \text{ atm} = 20265 \text{ Pa}$$

Partial pressure of nitrogen;

$$[1 \text{ atm} = 101325 \text{ Pa}]$$

$$p_{\text{N}_2} = 0.8 \text{ atm} = 81060 \text{ Pa}$$

Using Henry's law equation

$$\chi = \frac{P}{K_H}$$

 \therefore Mole fraction of O_2 in water

$$\chi_{\text{O}_2} = \frac{p_{\text{O}_2}}{K_{\text{H}(\text{O}_2)}} = \frac{20265}{2 \times 10^9} = 10.13 \times 10^{-6}$$

Mole fraction of N_2 in water

$$\chi_{\text{N}_2} = \frac{p_{\text{N}_2}}{K_{\text{H}(\text{N}_2)}} = \frac{81060}{5 \times 10^9} = 16.212 \times 10^{-6}$$

$$\therefore \frac{\text{Mole of dissolved oxygen}}{\text{Mole of dissolved nitrogen}} = \frac{10.13 \times 10^{-6}}{16.212 \times 10^{-6}} = 0.62$$

$$\text{Hence, amount percent of } \text{O}_2 = \frac{0.62}{1.62} \times 100 = 38.27\%$$

$$\text{Amount percent of } \text{N}_2 = 100 - 38.27 = 61.73\%$$

ILLUSTRATION 2.7

State Henry's law. What is the significance of K_H ?

Sol. **Henry's law:** It states that "the partial pressure of a gas in vapour phase (p) is proportional to the mole fraction of the gas (χ) in the solution" and is expressed as

$$p = K_H \chi$$

where K_H is Henry's law constant.

Significance of K_H : As $p_A = K_H \chi_A$. Thus, at constant temperature for the same partial pressure of different gases, $\chi_A \propto 1/K_H$. In other words solubility is inversely proportional to Henry's constant of the gas. Higher the value of K_H , lower is the solubility of the gas. As H_2 is more soluble than helium, H_2 will have lower value of K_H than that of helium.

APPLICATIONS OF HENRY'S LAW

Henry's law finds several applications in industry and explains some biological phenomena. Notable among these are:

- To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.
- To minimize the painful effects accompanying the decompression of deep sea divers, oxygen diluted with less soluble helium gas is used as breathing gas.
- In lungs, where oxygen is present in air with high partial pressure, haemoglobin combines with oxygen to form oxy-haemoglobin. In tissues where the partial pressure of oxygen is low, oxohaemoglobin releases oxygen for utilization in cellular activities.
- Scuba divers must cope with high concentrations of dissolved gases while breathing air at high pressure underwater. Increased pressure increases the solubility of atmospheric gases in blood. When the divers come towards surface, the pressure gradually decreases. This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as bends, which are painful and dangerous to life. To avoid bends as well as the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).
- At high altitudes the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of climbers or people living at high altitudes. Low blood oxygen causes climbers to become weak and makes them unable to think clearly, symptoms of a condition known as anoxia.

LIMITATIONS OF HENRY'S LAW

Henry's law is valid only when

- Pressure is low.
- Temperature is low.
- The gas is not highly soluble.

- The gas neither reacts chemically with the solvent nor dissociates or associates in the solvent.

Note: The effect of temperature on the solubility of gases in liquids decreases with rise in temperature. When dissolved, the gas molecules are present in liquid phase and the process of dissolution can be considered similar to condensation and heat is evolved in this process. As dissolution is an exothermic process, the solubility should decrease with increase of temperature.

2.5 SOLUBILITY OF A SOLID IN A LIQUID

The solubility of solids in liquids varies with the nature of solid and liquid, temperature, and to a lesser extent on the pressure of the system. In general, a solute dissolves in a solvent if the intermolecular interactions are similar in the two or we may say like dissolves like.

When a solid solute is added to the solvent, some solute dissolves and concentration increases in solution. This process is called as *dissolution*. Some solute particle in solution collide with the solid solute particle and get separated out of solution. This process is known as *crystallization*. At equilibrium both dissolution and crystallization occur at the same rate at constant temperature and pressure. At this stage the concentration of solute in solution remains constant under the condition of constant temperature and pressure.

The solution at this stage in which no more solute can be dissolved at the same temperature and pressure is called *saturated solution*. An unsaturated solution is one in which more solute can be dissolved at same temperature and pressure. The maximum amount of solute that can be dissolved by the solvent at a particular temperature is called its *solubility*. Thus, the solubility of any substance at a given temperature is defined as the amount of the substance that dissolves in 100 g of the solvent at a given temperature to form a saturated solution.

Solubility of one substance into another depends on the nature of the substance. In addition to these, temperature and pressure also control this phenomenon. Temperature has a significant effect on the solubility of a solid substance into a solvent. The solubility may increase or decrease with increase in temperature. According to the Le Chatelier's principle, if the dissolution process is endothermic ($\Delta_{\text{sol}}H > 0$), the solubility should increase with rise in temperature and if the process is exothermic the solubility should decrease, e.g., the solubility of sodium chloride ($NaCl$), potassium chloride (KCl), potassium iodide (KI), increases with rise in temperature, while solubility of calcium carbonate ($CaCO_3$) and lithium sulphate (Li_2SO_4) decreases with rise in temperature.

However, for some substances the solubility increases upto a certain temperature and then decreases with further rise in temperature. For these substances solubility behaviour not regular. For example, the solubility of sodium sulphate (Na_2SO_4) increases upto $32.8^\circ C$ and above it the solubility decreases. This temperature corresponding to the break in the solubility curve is known as *transition temperature*. At transition temperature there is an equilibrium between sodium decahydrate $Na_2SO_4 \cdot 10H_2O$ and

anhydrous sodium sulphate (Na_2SO_4). Above this temperature only anhydrous sodium sulphate exists while below this temperature hydrated form exists.

Pressure does not have any marked effect on the solubility of solids in liquids. It is so because solids and liquids are highly incompressible and practically remain unaffected by change in pressure.

2.6 VAPOUR PRESSURE OF LIQUID SOLUTION

Vapour pressure of a volatile liquid: Let us consider a liquid placed in a beaker and is covered with a jar (Fig. 2.6). The volatile liquid evaporates and occupy the space available in jar with its vapour. In the jar above the liquid surface the vapour molecules are in random motion; they collide with each other and get condensed into liquid, and eventually an equilibrium would be established between vapour phase and liquid phase. Thus, both evaporation and condensation processes go on simultaneously. The pressure exerted by the vapour molecules on the surface of liquid in the jar at equilibrium is called *vapour pressure*. Thus, the pressure exerted by the vapour above the liquid surface at equilibrium at a given temperature is called vapour pressure.

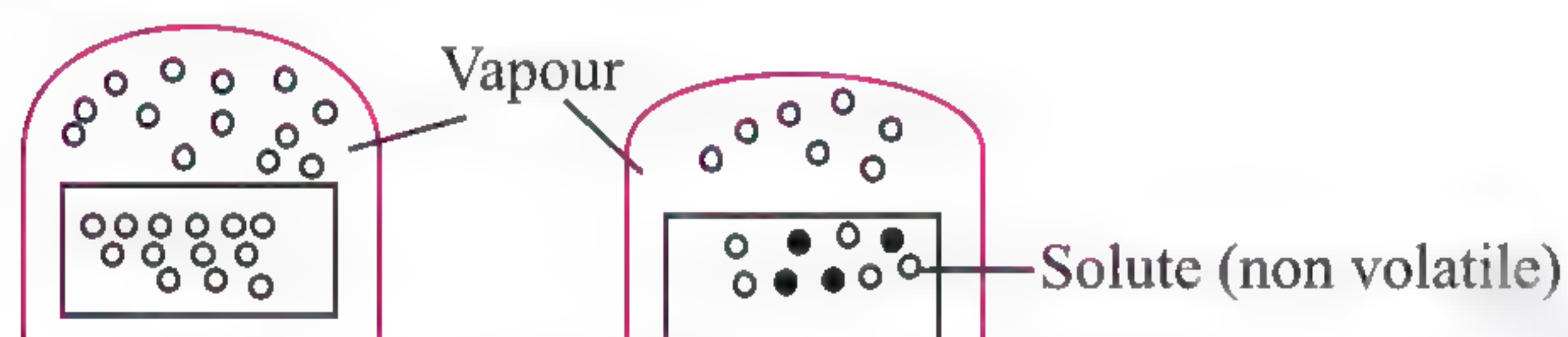


Fig. 2.6 (a) Pure solvent and (b) solvent and solute

The vapour pressure of liquid depends upon following parameters:

- **Temperature:** The vapour pressure of a liquid increases with increase in temperature. This is because on increasing the temperature the kinetic energy of molecules increases that results into the fact that more molecules escape from the surface of the liquid into the vapour phase resulting in higher vapour pressure.
- **Nature of liquid:** Every liquid has a different magnitude of intermolecular force. The liquids with weaker intermolecular forces tend to easily escape from liquid phase to vapour phase and hence they have higher vapour pressure, while those liquids which have strong intermolecular forces do not easily get vapourized so they have less vapour pressure.

Vapour pressure of solution containing volatile solvent in nonvolatile solute: In such solution only solvent molecules get vapourized and vapour pressure is solely from the solvent alone. This vapour pressure of the solution is found to be lower than the vapour pressure of pure solvent.

In the solution, the surface has both solute and solvent molecules, thereby a fraction of the surface covered by the solvent molecules gets reduced. Consequently, the number of solvent molecules escaping from the surface is correspondingly reduced, thus the vapour pressure is also reduced. The decrease in the vapour pressure of solvent is directly proportional to the quantity of solute present in the solution irrespective of its

nature. For example, decrease in the vapour pressure of water by adding 1.0 mole of sucrose to 1 kg of water is nearly same to that produced by adding 1.0 mole of urea to the same quantity of water at the same temperature.

2.7 RAOULT'S LAW

The French chemist Francois Marie Raoult in 1886 observed that the partial vapour pressure of a solvent over a solution of a nonvolatile solute, p_{solution} is directly proportional to the mole fraction of the solvent in the solution (Fig. 2.7)

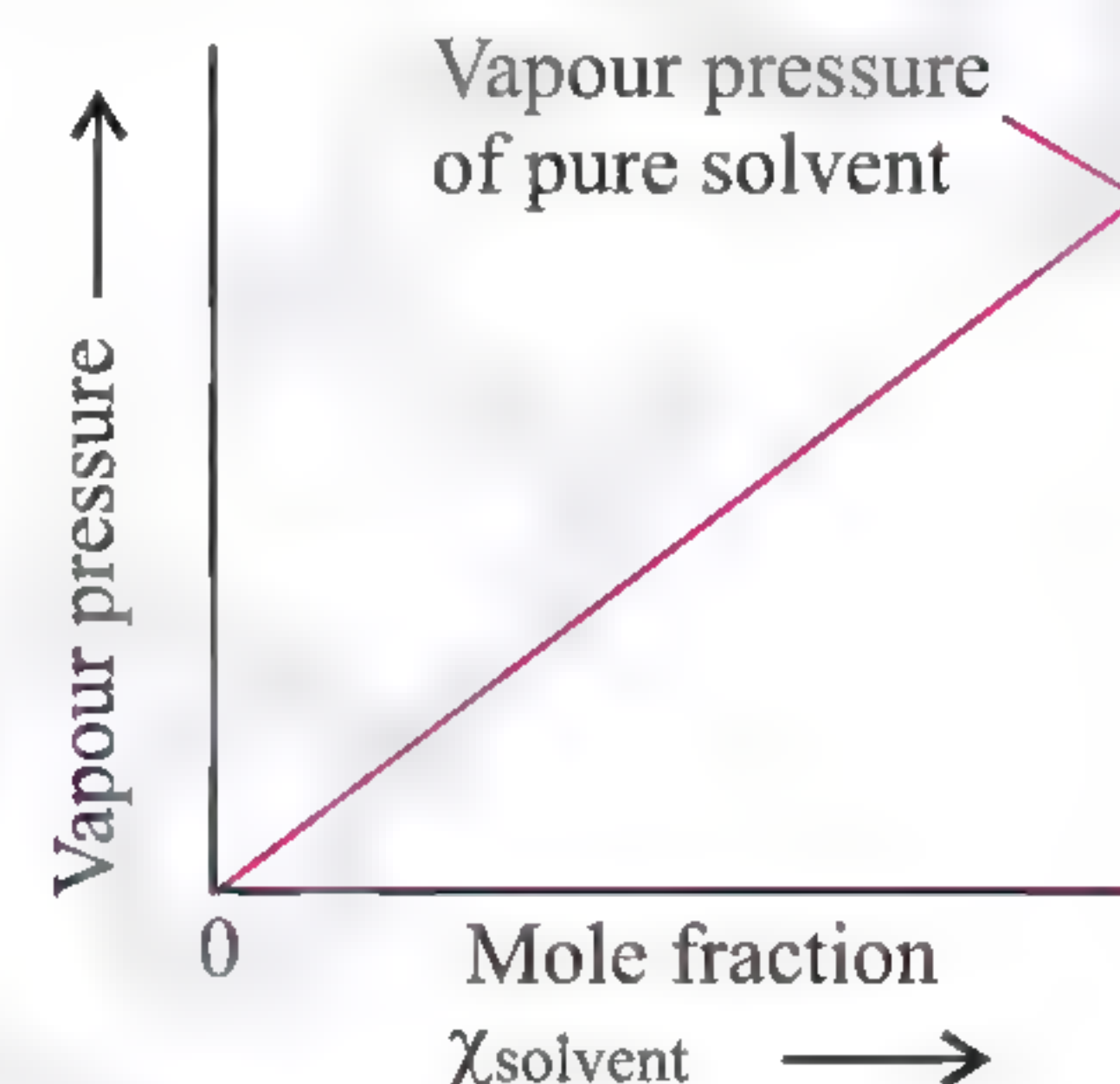


Fig. 2.7 If a solution obeys Raoult's law for all concentrations, its vapour pressure would vary linearly from zero to the vapour pressure of the pure solvent

Mathematically, such a relationship is described as

$$p_{\text{solution}} = \chi_{\text{solvent}} p_{\text{solvent}}^{\circ} \quad \dots(i)$$

where $p_{\text{solvent}}^{\circ}$ is the vapour pressure of the pure solvent at the given temperature. This relationship is known as Raoult's law, and the rearrangement of Eq. (i) gives

$$\frac{p_{\text{solution}}}{p_{\text{solvent}}^{\circ}} = \chi_{\text{solvent}} \quad \dots(ii)$$

Thus, Raoult's law may be defined as: *at a given temperature, the vapour pressure of a solution containing nonvolatile solute is directly proportional to the mole fraction of the solvent.*

2.7.1 RAOULT'S LAW AS A SPECIAL CASE OF HENRY'S LAW

According to Raoult's law, the vapour pressure of a volatile component in a given solution is given by $P_A = P_A^{\circ} \chi_A$. In the solution of a gas in a liquid, the gaseous component is so volatile that it exists as a gas and we have already seen that its solubility is governed by Henry's law that states that $P = K_H \chi$.

If we compare the equations for Raoult's law and Henry's law, it can be seen that the partial pressure of the volatile component or gas is directly proportional to its mole fraction in solution. Only the proportionality constant K_H differs from P_A° . Thus, Raoult's law becomes a special case of Henry's law in which K_H becomes equal to P_A° . Even in liquid solution, sometimes one of the components may obey Henry's law over a range of mole fraction. In practice, in the solution in which the solute behaves ideally according to Henry's law the solvent also behaves ideally according to Raoult's law (though the reverse is not necessarily true and Raoult's law ideality on the part of the solvent does not mean that the solute must obey Henry's law).

As a real solution approaches the limit of infinite dilution its components behave more ideal. The solvent obeys Raoult's law whereas solute (minor component) obeys Henry's law for dilute

solutions. This can be explained with the help of a systematic diagram given below (Fig. 2.8).

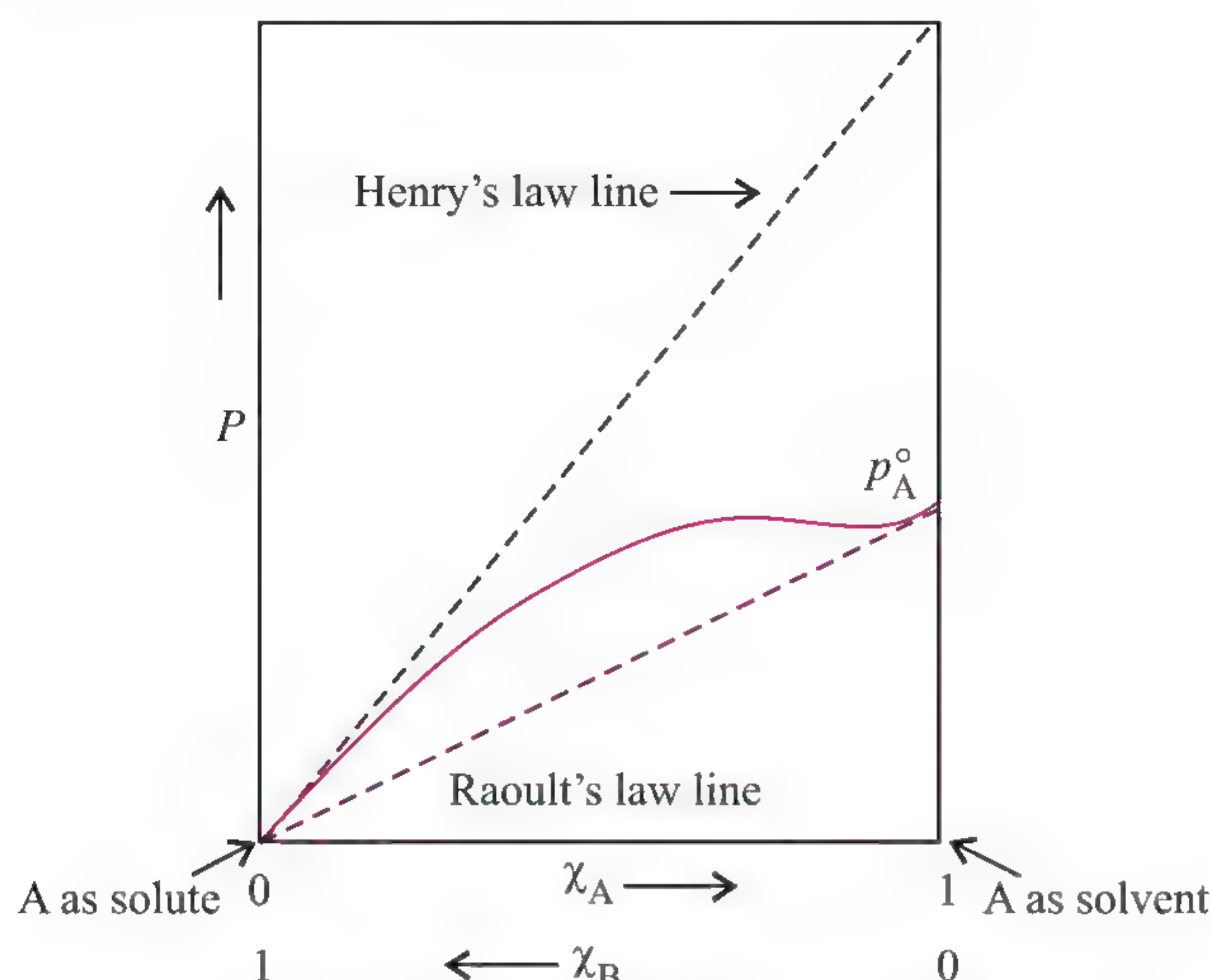


Fig. 2.8 Schematic graph indicating the applicability of Henry's law to the solute and Raoult's law to the solvent

In Fig. 2.8, we have a solution of liquids A and B. The partial pressure of A is plotted against its mole fraction in the solution, hence we get a curve as shown in Fig. 2.8. The curve according to Raoult's law can be obtained by connecting the zero point at the left ($\chi_A = 0$) with the point representing p_A^0 at the right ($\chi_A = 1$). It can be seen from Fig. 2.8 that Raoult's law curve meets the partial vapour pressure curve tangentially in the region where $\chi_A \rightarrow 1$. Thus, we see that Raoult's law is applicable only in the limited range of concentration where A is present in excess amount and is thus acting as a solvent. Now if we draw Henry's law curve and extrapolate this line to the right axis, where $\chi_A = 1$, gives a hypothetical vapour pressure which would be observed only if Henry's law is applicable over the entire range of concentration, that is up to $\chi_A = 1$. Therefore, from Henry's law curve we observe that it meets to partial pressure curve only upto a small range at which A acts as solute ($\chi_A \approx 0$).

2.7.2 RAULT'S LAW FOR A SOLUTION CONTAINING VOLATILE COMPONENTS

What happens when the solute and solvent both are volatile? Here, the vapour phase consists of vapours of both the components of the solution. The partial vapour pressure of each component of the solution depends on the mole fraction of the corresponding component. Let us consider a solution in which both the components obey Raoult's law marked as A and B with their mole fractions χ_A and χ_B , respectively. Their partial vapour pressures p_A and p_B are proportional to the respective mole fractions in the solutions.

Thus, $p_A \propto \chi_A$

Similarly, $p_B \propto \chi_B$

Based on experimental findings, Raoult proposed that in case of mixture of two miscible liquids, the above relation written as follows holds good:

$$p_A = p_A^0 \chi_A \quad \dots(i)$$

$$p_B = p_B^0 \chi_B \quad \dots(ii)$$

where p_A^0 and p_B^0 represent the vapour pressures of pure components A and B, respectively. The relationship between

the vapour pressure of a component and its mole fraction is another form of Raoult's law. This can be stated as: *for a solution of volatile liquids, the partial pressure of each component in the solution is directly proportional to its mole fraction*. The law is applicable only when the two volatile liquids form a homogeneous solution.

A plot of p_A and p_B against χ_A or χ_B for a solution should give a straight line (Fig. 2.9).

These lines pass through points p_A^0 or p_B^0 when χ_A and χ_B equals unity. According to Dalton's law of partial pressure, the total pressure of the solution for any composition is given as

$$p_{\text{total}} = p_A + p_B \quad \dots(iii)$$

Here p_{total} is indicated in Fig. 2.9 by line III, obtained by joining the points p_A^0 and p_B^0 .

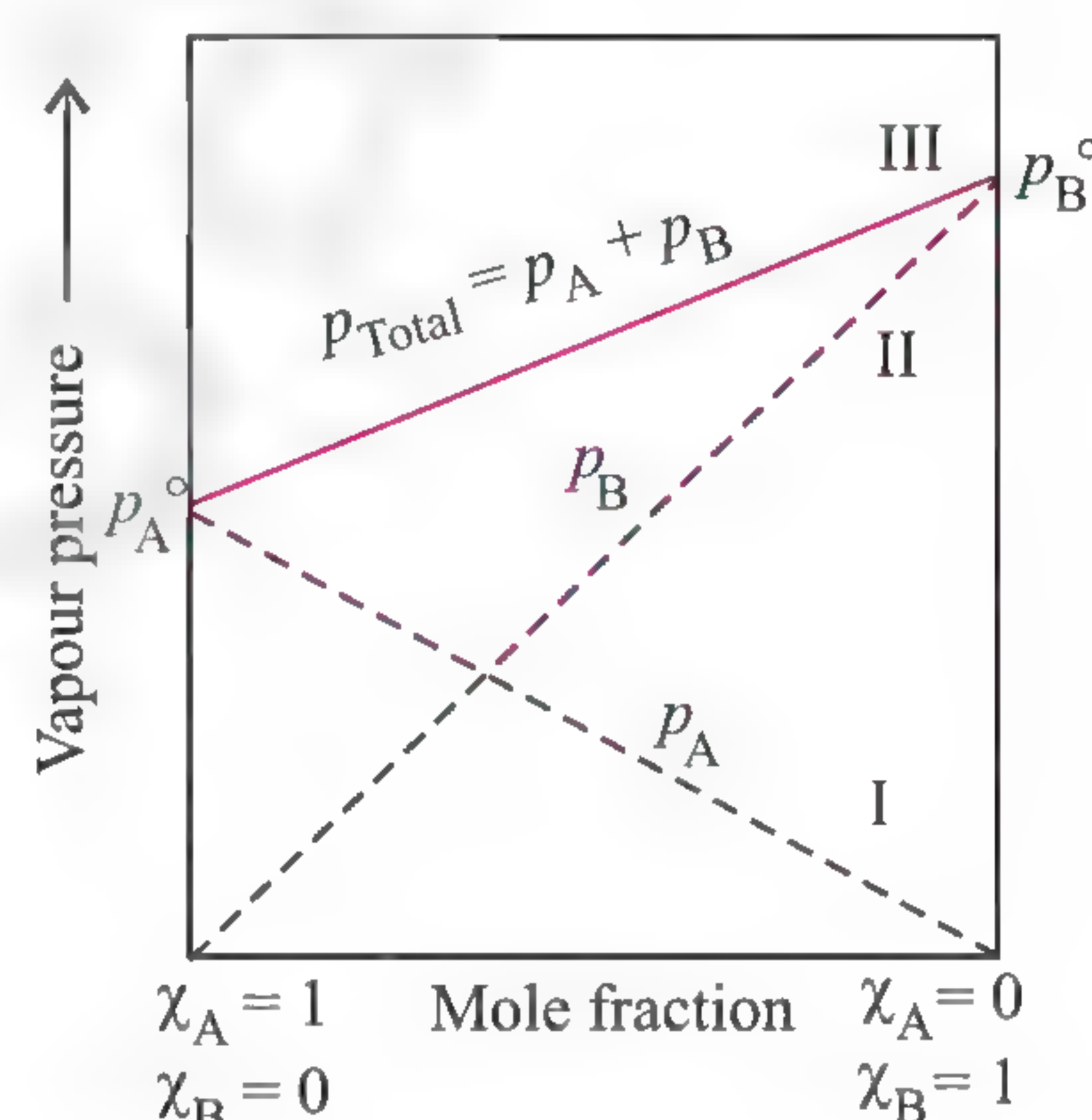


Fig. 2.9 The relationship between vapour pressure and mole fraction of an ideal solution at constant temperature. The dashed lines I and II represent the partial pressure of the components. (It can be seen from the plot that p_A and p_B are directly proportional to χ_A and χ_B , respectively). The total vapour pressure is given by line III in the figure.

Solutions obeying Raoult's law are called *ideal liquid solutions*. Evidently for such solutions, the vapour pressure are intermediate between the values, p_A and p_B and they all lie on the straight line joining p_A^0 and p_B^0 .

Substituting the values of p_A and p_B in Eq. (iii), we get

$$p_{\text{total}} = \chi_A p_A^0 + \chi_B p_B^0 \quad \dots(iv)$$

$$\begin{aligned} &= (1 - \chi_B) p_A^0 + \chi_B p_B^0 \\ &= p_A^0 + (p_B^0 - p_A^0) \chi_B \end{aligned} \quad \dots(v)$$

Following conclusions can be drawn from Eq. (v):

- Total vapour pressure over the solution can be related to the mole fraction of any one components.
- Total vapour pressure over the solution varies linearly with the mole fraction of component B.
- Depending on the vapour pressures of the pure components A and B, the total vapour pressure over the solution decreases or increases with the increase of the mole fraction of component A.

The plot [line III (Fig. 2.9)] of p_{total} has minimum value of p_A^0 and maximum value is p_B^0 , assuming that component A is less volatile than component B, i.e., $p_A^0 < p_B^0$.

[The composition of vapour phase can be determined with the help of Dalton's law of partial pressure.]

Let χ_A^V and χ_B^V be mole fractions of components A and B, respectively, in the vapour phase. Using Dalton's law of partial pressure:

$$p_A = \chi_A^V p_{\text{total}}$$

$$\text{and } p_B = \chi_B^V p_{\text{total}}$$

$$\text{or } \chi_A^V = \frac{p_A}{p_{\text{total}}} = \frac{\chi_A p_A^\circ}{p_B^\circ + (p_A^\circ - p_B^\circ) \chi_A}$$

$$\chi_B^V = 1 - \chi_A^V = \frac{\chi_B p_B^\circ}{p_A^\circ + (p_B^\circ - p_A^\circ) \chi_B}$$

2.8 IDEAL AND NON-IDEAL SOLUTIONS

Binary solutions are classified into two categories: ideal solutions and non-ideal solutions.

1. Ideal solution:

A solution which obeys Raoult's law exactly at all range of concentration and temperature is known as ideal solution. In such solution the two components are identical in molecular size, shape, and have almost identical intermolecular forces. In these solutions, the intermolecular interaction between the unlike molecules (A–B) are of same magnitude as the intermolecular interaction between the like molecules, i.e., (A–A) and (B–B).

Then according to Raoult's law the partial pressure of two components of the solution is given as: $p_A = \chi_A p_A^\circ$ and $p_B = \chi_B p_B^\circ$. According to Dalton's law of partial pressure, the total pressure is given as $p_t = p_A + p_B$ or $p_t = \chi_A p_A^\circ + \chi_B p_B^\circ$.

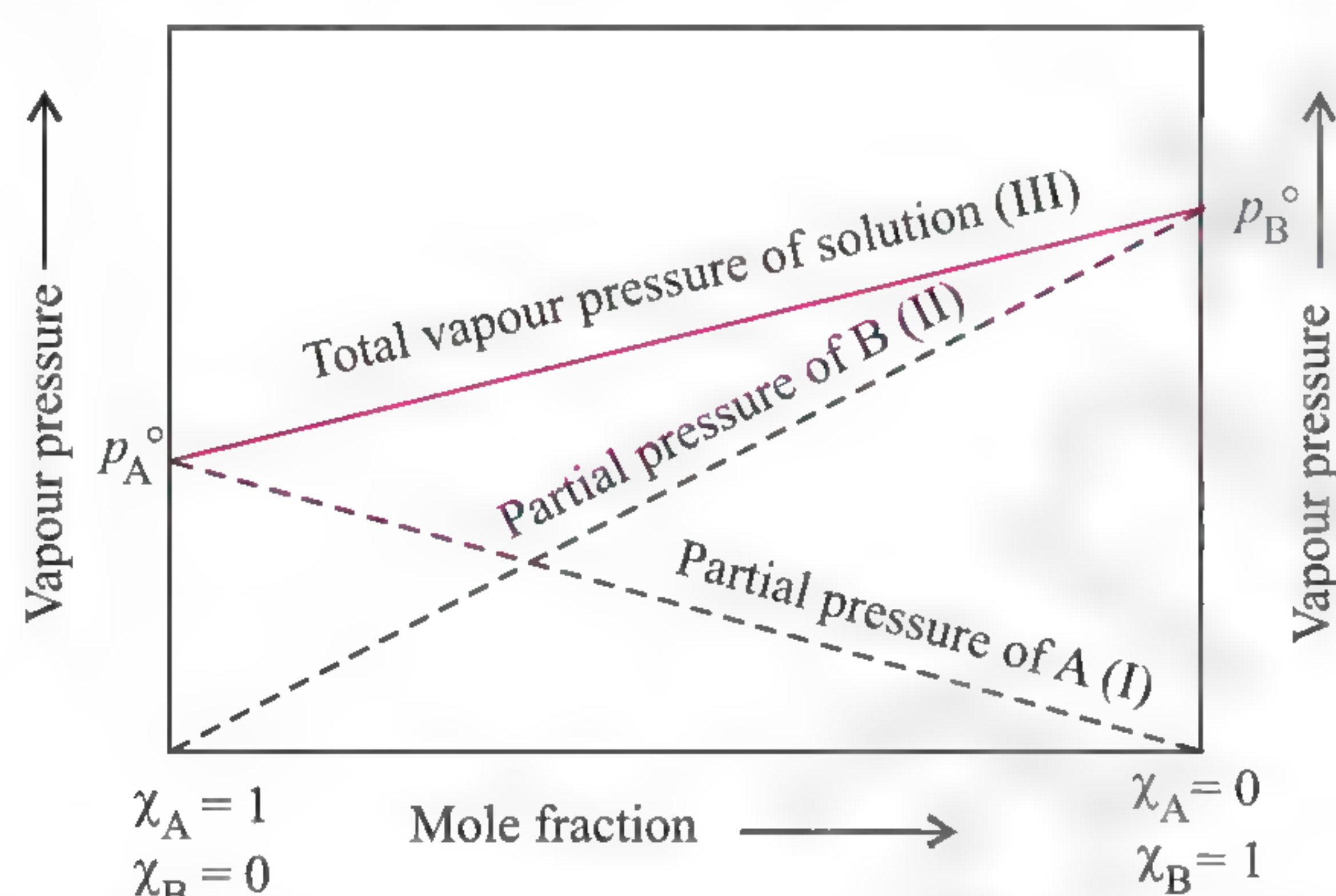


Fig. 2.10 Vapour pressure behaviour of ideal solutions obeying Raoult's law. The dashed lines I and II represent the partial vapour pressure of the components. The total vapour pressure is given by line III (solid line)

The total pressure p_t is shown by line III in Fig. 2.10 obtained by joining the points p_A° and p_B° . It is clear from the figure that the vapour pressure of the solutions of different compositions, in case of ideal solutions, lies between the vapour pressure of the pure components (p_A° and p_B°).

Ideal solutions have two important properties:

- Enthalpy of mixing ($\Delta_{\text{mix}}H$):** The enthalpy of mixing of pure components to form the solution is zero. It means that no heat is absorbed or evolved when the components are mixed, i.e., ($\Delta_{\text{mix}}H = 0$) because there is no change in magnitude of the attractive forces in the two components present.
- Volume of mixing ($\Delta_{\text{mix}}V$):** In ideal solution, the change in volume on mixing is zero, i.e., $\Delta_{\text{mix}}V = 0$. In such solution the volume of the solution is the sum of the volume of the components before mixing.

A perfectly ideal solution is rare but some solutions are nearly ideal in behaviour. Examples of ideal solution are: (i) solution of *n*-hexane and *n*-heptane, (ii) benzene and toluene, (iii) ethyl bromide and ethyl chloride, (iv) chlorobenzene and bromobenzene, (v) benzene and xylene, (vi) ethylene dichloride ($\text{ClCH}_2\text{CH}_2\text{Cl}$) and ethylene dibromide ($\text{BrCH}_2\text{CH}_2\text{Br}$), (vii) $\text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{OH}$, and (viii) $\text{SnCl}_4 + \text{CCl}_4$.

2. Non-ideal solution:

A solution which does not obey Raoult's law is known as non-ideal solution.

$$p_A \neq \chi_A p_A^\circ \text{ and } p_B \neq \chi_B p_B^\circ$$

In case of a non-ideal solution, the change in enthalpy of mixing ($\Delta_{\text{mix}}H$) and change in volume on mixing ($\Delta_{\text{mix}}V$) is not zero. The vapour pressure of such a solution is either higher or lower than that predicted by Raoult's law. If it is higher, the solution exhibits *positive deviation* and if it is lower, it exhibits *negative deviation* from Raoult's law. The cause for these deviations lies in the nature of interaction at the molecular level.

3. Types of non-ideal solutions:

(a) *Non-ideal solutions showing positive deviation from Raoult's law:* If in a binary solution of two components A and B, the interaction between the unlike components A–B are weaker than the interaction between the like components A–A and B–B, this means that in such solutions molecules of A (or B) will find it easier to escape than in pure state. This will result in having greater vapour pressure of each component of the solution than expected on the basis of Raoult's law, and hence the total vapour pressure will also be higher than in the case of ideal solution. This type of behaviour of solution is defined as *positive deviation* from Raoult's law.

In Fig. 2.11(a), a solution is exhibiting positive deviation. In such solution $p_A > \chi_A p_A^\circ$ and $p_B > \chi_B p_B^\circ$ and $p_{\text{total}} > \chi_A p_A^\circ + \chi_B p_B^\circ$.

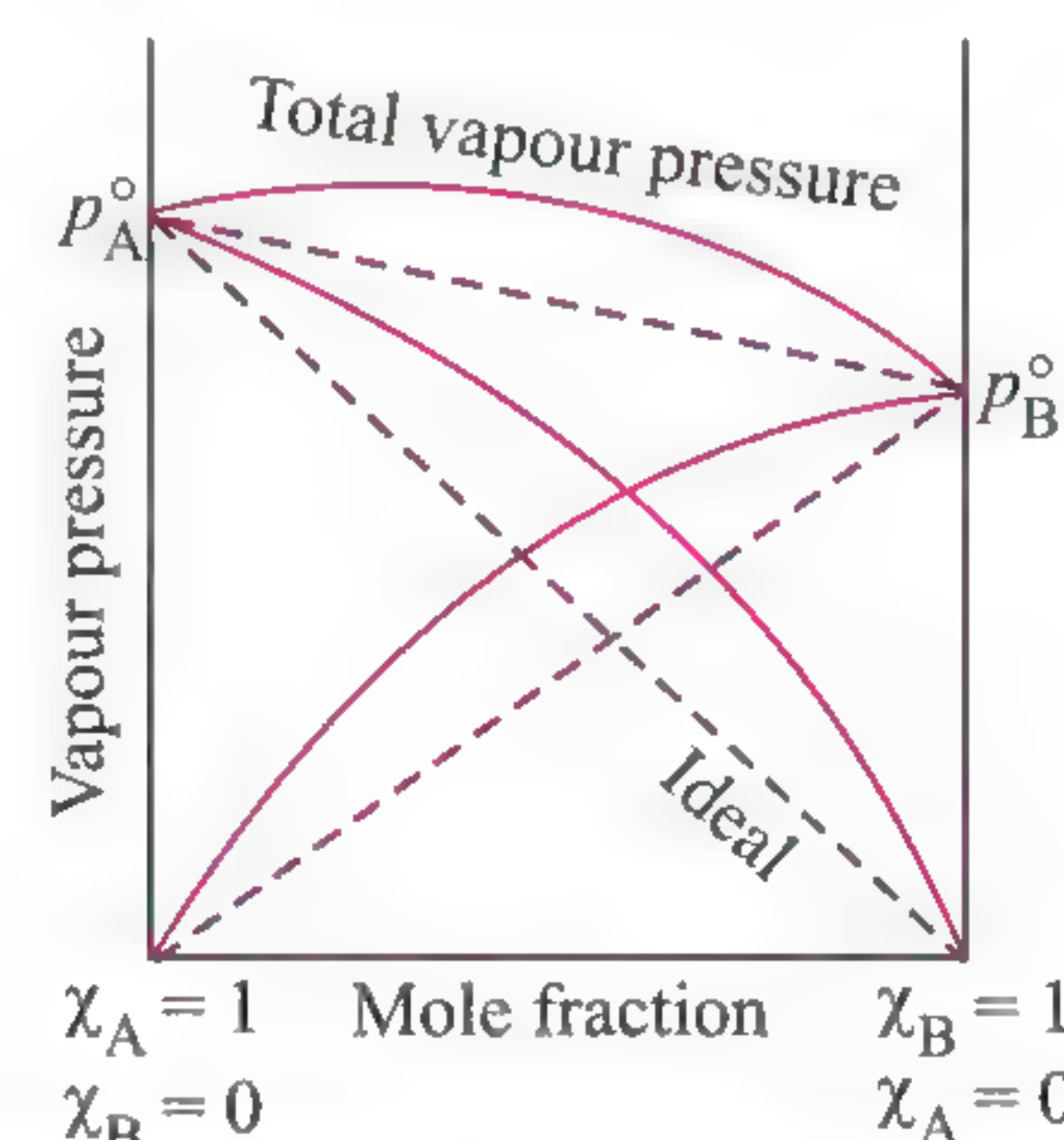
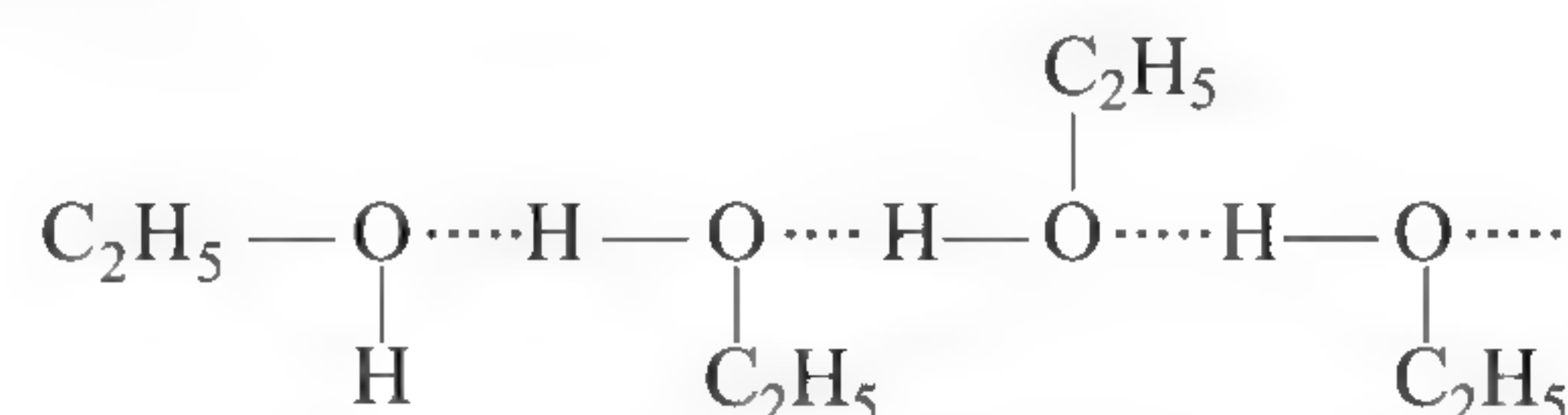


Fig. 2.11(a) Positive deviation from ideal behaviour. Dotted line represents ideal solution and dark line for non-ideal solution

A solution of ethanol and acetone behave in this way. In pure ethanol, molecules are held together with hydrogen bond as shown below.



On adding acetone, the molecules of acetone get in between the host molecules breaking the hydrogen bonds of host molecules, this causes to weaken the intermolecular attraction between the alcohol molecules. This results into an increase in the escaping tendency of alcohol and acetone molecules from the solution. Consequently, the vapour pressure of the solution is greater than the vapour pressure expected from Raoult's law.

In such solution $\Delta_{\text{mix}}H$ is positive because energy is required to break A–A and B–B bonds. For such solutions, the dissolution process is endothermic, i.e., the solubility will increase with increase in temperature. $\Delta_{\text{mix}}V$ is also positive for such solution because there is decrease in the magnitude of intermolecular forces in the solution, the molecules are loosely held, and therefore the volume of mixing increases.

Few examples of solution that shows positive deviation are:

- Ethyl alcohol and cyclohexane
- Acetone and carbon disulphide
- Benzene and acetone
- Carbon tetrachloride and chloroform
- Ethyl alcohol and water
- Acetone and ether

(b) *Non-ideal solution showing negative deviation from Raoult's law*: In such solution the interaction between the unlike molecules A–B is stronger than the interaction between the like ones, i.e., A–A and B–B. In the solution, molecules of A and B are strongly held due to stronger A–B interaction and therefore the escaping tendency of molecules of A or B becomes less than that of pure liquid. Consequently, each component has lesser partial pressure than that expected from Raoult's law. As a result, the total vapour pressure is less than that of ideal solution. These type of solutions are said to have *negative deviation* from Raoult's law.

Figure 2.11(b) shows a solution exhibiting negative deviation. In such solution $p_A < \chi_A p_A^\circ$ and $p_B < \chi_B p_B^\circ$ and $p_{\text{total}} < \chi_A p_A^\circ + \chi_B p_B^\circ$.

For example, a solution of chloroform and acetone shows negative deviation from Raoult's law. This is because in the solution the chloroform molecule is able to form hydrogen bond with the acetone molecule as shown below.

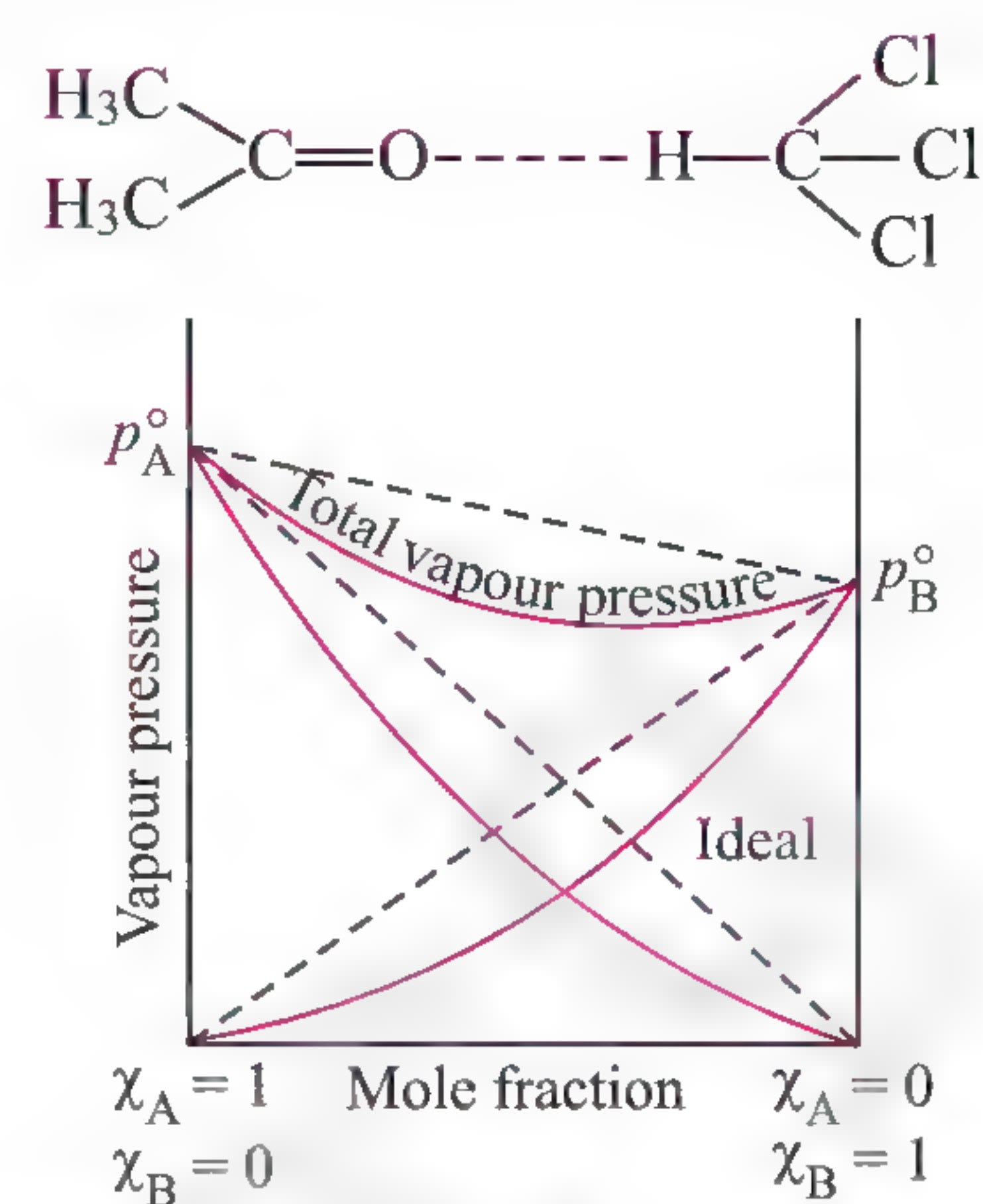


Fig. 2.11(b) Negative deviation from ideal behaviour. Dotted line represents ideal solution and dark line represents non-ideal solution

This newly formed hydrogen bond in the solution between the molecules of acetone and chloroform is stronger and decreases the escaping tendency of the liquid molecules from the solution. Consequently the vapour pressure decreases resulting in negative deviation from Raoult's law. In this type of solution, $\Delta_{\text{mix}}H$ is negative because on the formation of new attractive forces energy is released. Therefore, the dissolution process is exothermic and on heating the solubility of solution will decrease.

$\Delta_{\text{mix}}V$ is also negative in such solution because on the formation of new attractive forces molecules comes closer to each other and are held more strongly. That results in the decrease in the volume on mixing, i.e., $\Delta_{\text{mix}}V$ is negative.

Few more examples of solution that show negative deviation are: acetone and chloroform, acetone and aniline, H_2O and HNO_3 , chloroform and nitric acid, chloroform and diethyl ether, H_2O and HCl , H_2O and H_2SO_4 , $(\text{H}_2\text{O} + \text{HNO}_3)$, CH_3OH and CH_3COOH , and $\text{CH}_3\text{COOCH}_3$ and CHCl_3 .

In Table 2.2, difference between ideal and non-ideal solutions is illustrated.

4. Mole fraction of solvent (A) in vapour phase = $\chi_A^V = \frac{p_A}{P_{\text{Total}}}$

Table 2.2 Comparison between ideal and non-ideal solutions

Ideal solutions	Non-ideal solutions	
	Positive deviation from Raoult's law	Negative deviation from Raoult's law
a. Obey Raoult's law at every range of concentration.	a. Do not obey Raoult's law.	a. Do not obey Raoult's law.
b. $\Delta_{\text{mix}}V = 0$; total volume of solution is equal to the sum of volumes of the components.	b. $\Delta_{\text{mix}}V > 0$. Volume is increased after dissolution.	b. $\Delta_{\text{mix}}V < 0$. Volume is decreased during dissolution.
c. $\Delta_{\text{mix}}H = 0$; neither heat is evolved nor absorbed during dissolution.	c. $\Delta_{\text{mix}}H > 0$. Endothermic dissolution; heat is absorbed.	c. $\Delta_{\text{mix}}H < 0$. Exothermic dissolution; heat is evolved.
d. A–A, A–B, B–B interactions should be same, i.e., A and B are identical in shape, size, and character.	d. A–B attractive force should be weaker than A–A and B–B attractive forces. A and B have different shape, size	d. A–B attractive force should be greater than A–A and B–B attractive forces A and B have different shape, size and character.
e. $p = p_A + p_B = p_A^\circ \chi_A + p_B^\circ \chi_B$ i.e., $p_A = p_A^\circ \chi_A$; $p_B = p_B^\circ \chi_B$	e. $p_A > p_A^\circ \chi_A$; $p_B > p_B^\circ \chi_B$ $\therefore p_A + p_B > p_A^\circ \chi_A + p_B^\circ \chi_B$	e. $p_A < p_A^\circ \chi_A$; $p_B < p_B^\circ \chi_B$ $\therefore p_A + p_B < p_A^\circ \chi_A + p_B^\circ \chi_B$

f. Escaping tendency of A and B should be same in pure liquids and in the solution.	f. A and B escape easily showing higher vapour pressure than the expected value.	f. Escaping tendency of both components A and B is lowered showing lower vapour pressure than expected ideally.
Examples Dilute solutions Benzene + Toluene <i>n</i> -Hexane + <i>n</i> -Heptane Chlorobenzene + Bromobenzene Ethyl bromide + Ethyl iodide <i>n</i> -Butyl chloride + <i>n</i> -Butyl bromide	Examples Acetone + Ethanol Acetone + CS ₂ Water + Methanol Water + Ethanol CCl ₄ + Toluene CCl ₄ + CHCl ₃ Acetone + Benzene CCl ₄ + CH ₃ OH Cyclohexane + Ethanol	Examples Acetone + Aniline Acetone + Chloroform CH ₃ OH + CH ₃ COOH H ₂ O + CH ₃ COOH Chloroform + Diethyl ether H ₂ O + HCl, H ₂ O + H ₂ SO ₄ , H ₂ O + HNO ₃ Acetic acid + Pyridine Chloroform + Benzene CH ₃ COOH + CHCl ₃

ILLUSTRATION 2.8

Why does the use of pressure cooker reduce cooking time?

Sol. At higher pressure over the liquid due to weight of the pressure cooker lid, the liquid starts boiling at higher temperature. Therefore, cooking occurs faster.

ILLUSTRATION 2.9

Why is the vapour pressure of a liquid constant at a constant temperature?

Sol. Vapour pressure is the pressure of the vapour at equilibrium state when the rate of evaporation becomes equal to the rate of condensation. The equilibrium constant does not change at a particular temperature and therefore the vapour pressure remains constant.

ILLUSTRATION 2.10

Two liquids A and B are mixed and the resulting solution is found to be cooler. What do you conclude about the deviation from ideal behaviour?

Sol. The solution shows positive deviation from ideal behaviour.

ILLUSTRATION 2.11

The dissolution of ammonium chloride in water is an endothermic process. What is the effect of temperature on its solubility?

Sol. Since solubility of NH₄Cl in water is an endothermic process, its solubility increases with rise in temperature (Le Chatelier's principle).

ILLUSTRATION 2.12

Mixing of acetone with chloroform takes place with reduction in volume? What type of deviation from Raoult's law is shown in this case?

Sol. The solution has negative deviation from Raoult's law because decrease in volume indicates strong forces of interaction between the molecules in solution.

ILLUSTRATION 2.13

CCl₄ and water are immiscible whereas ethanol and water are miscible in all proportions. Correlate this behaviour with molecular structure of these compounds.

Sol. CCl₄ is a non-polar covalent compound, whereas water is a polar compound. CCl₄ can neither form H-bonds with water molecules nor can it break H-bonds in water molecules. Therefore, it is insoluble in water.

Ethanol is a polar compound and can form H-bonds with water, which is a polar solvent. Therefore, it is miscible with water in all proportions.

ILLUSTRATION 2.14

Vapour pressure of pure A (p_A°) = 100 mm Hg

Vapour pressure of pure B (p_B°) = 150 mm Hg

2 mol of liquid A and 3 mol of liquid B are mixed to form an ideal solution. The vapour pressure of solution will be:

- a. 185 mm b. 130 mm
c. 148 mm d. 145 mm

Sol. b. $\chi_A = \frac{2}{5}$, $\chi_B = \frac{3}{5}$;

Using Raoult's law equation,

$$P_{\text{total}} = p_A^\circ \chi_A + p_B^\circ \chi_B$$

$$= 100 \times \frac{2}{5} + 150 \times \frac{3}{5} = 40 + 90 = 130$$

ILLUSTRATION 2.15

The vapour pressure of pure benzene at 88°C is 957 mm and that of toluene at the same temperature is 379.5 mm. The composition of benzene–toluene mixture boiling at 88°C will be

- a. $\chi_{\text{benzene}} = 0.66$; $\chi_{\text{toluene}} = 0.34$
b. $\chi_{\text{benzene}} = 0.34$; $\chi_{\text{toluene}} = 0.66$
c. $\chi_{\text{benzene}} = \chi_{\text{toluene}} = 0.5$
d. $\chi_{\text{benzene}} = 0.75$; $\chi_{\text{toluene}} = 0.25$

Sol.

$$a. p = p_{\text{benzene}}^{\circ} \chi_{\text{benzene}} + p_{\text{toluene}}^{\circ} \chi_{\text{toluene}}$$

$$760 = 957 \chi_{\text{benzene}} + 379.5(1 - \chi_{\text{benzene}})$$

$$\chi_{\text{benzene}} = 0.66$$

$$\text{and } \chi_{\text{toluene}} = 1 - 0.66 = 0.34$$

ILLUSTRATION 2.16

The vapour pressure of a certain pure liquid A at 298 K is 40 mbar. When a solution of B is prepared in A at the same temperature, the vapour pressure is found to be 32 mbar. The mole fraction of A in the solution is

- a. 0.5 b. 0.3
c. 0.4 d. 0.8

Sol.

$$d. p = p^{\circ} \chi_A$$

$$32 = 40 \times \chi_A \text{ or } \chi_A = 0.8$$

ILLUSTRATION 2.17

100 mL of liquid A and 25 mL of liquid B are mixed to form a solution of volume 125 mL. Then the solution is

- a. Ideal
b. Non-ideal with positive deviation
c. Non-ideal with negative deviation
d. Cannot be predicted

Sol.

$$a. \Delta_{\text{mix}} V = 0, \text{ hence the solution is ideal.}$$

ILLUSTRATION 2.18

An aqueous solution containing 28% by mass of liquid A (mol. mass = 140) has a vapour pressure of 160 mm at 30°C. Find the vapour pressure of the pure liquid A. (The vapour pressure of water at 30°C is 150 mm.)

Sol. For two miscible liquids,

$$P_{\text{total}} = \text{Mole fraction of A} \times p_A^{\circ} + \text{Mole fraction of B} \times p_B^{\circ}$$

$$\text{Number of moles of A} = \frac{28}{140} = 0.2$$

Liquid B is water. Its mass is (100 – 28), i.e., 72.

$$\text{Number of moles of B} = \frac{72}{18} = 4.0$$

$$\text{Total number of moles} = 0.2 + 4.0 = 4.2$$

$$\text{Given, } p_{\text{total}} = 160 \text{ mm}$$

$$p_B^{\circ} = 150 \text{ mm}$$

$$\text{So, } 160 = \frac{0.2}{4.2} \times p_A^{\circ} + \frac{4.0}{4.2} \times 150$$

$$p_A^{\circ} = \frac{17.15 \times 4.2}{0.2} = 360.15 \text{ mm}$$

Questions Based on Mole Fraction of Solvent in Vapour Phase (χ_A^V)**ILLUSTRATION 2.19**

The vapour pressures of ethanol and methanol are 44.0 mm and 88.0 mm Hg, respectively. An ideal solution is formed at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour.

Sol. Mol. mass of ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) = 46

$$\text{Number of moles of ethyl alcohol} = \frac{60}{46} = 1.304$$

$$\text{Mol. mass of methyl alcohol (CH}_3\text{OH)} = 32$$

$$\text{Number of moles of methyl alcohol} = \frac{40}{32} = 1.25$$

$$\text{Mole fraction of ethyl alcohol, } \chi_A = \frac{1.304}{1.304 + 1.25} = 0.5107$$

$$\text{Mole fraction of methyl alcohol, } \chi_B = \frac{1.25}{1.304 + 1.25} = 0.4893$$

$$\text{Partial pressure of ethyl alcohol} = \chi_A p_A^{\circ} = 0.5107 \times 44.0 = 22.47 \text{ mm Hg}$$

$$\text{Partial pressure of ethyl alcohol} = \chi_B p_B^{\circ} = 0.4893 \times 88.0 = 43.05 \text{ mm Hg}$$

$$\text{Total vapour pressure of solution} = 22.47 + 43.05 = 65.52 \text{ mm Hg}$$

Mole fraction of methyl alcohol in the vapour

$$= \frac{\text{Partial pressure of CH}_3\text{OH}}{\text{Total vapour pressure}} = \frac{43.05}{65.52} = 0.6570$$

ILLUSTRATION 2.20

Two liquids A and B form ideal solution. At 300 K, the vapour pressure of a solution containing 1 mol of A and 3 mol of B is 500 mm of Hg. At the same temperature, if one more mole of B is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Determine vapour pressures of A and B in their pure states.

Sol. Let the vapour pressure of pure A be $= p_A^{\circ}$; and the vapour pressure of pure B be $= p_B^{\circ}$.

$$\begin{aligned} \text{Total vapour pressure of solution (1 mol A + 3 mol B)} \\ = \chi_A p_A^{\circ} + \chi_B p_B^{\circ} \quad [\chi_A \text{ is mole fraction of A and } \chi_B \text{ is mole fraction of B}] \end{aligned}$$

$$500 = \frac{1}{4} p_A^{\circ} + \frac{3}{4} p_B^{\circ}$$

$$\text{or } 2000 = p_A^{\circ} + 3p_B^{\circ} \quad \dots(i)$$

Total vapour pressure of solution (1 mol A + 4 mol B)

$$= \frac{1}{5} p_A^{\circ} + \frac{4}{5} p_B^{\circ}$$

$$510 = \frac{1}{5} p_A^{\circ} + \frac{4}{5} p_B^{\circ}$$

$$2250 = p_A^\circ + 4p_B^\circ \quad \dots(ii)$$

Solving Eqs. (i) and (ii), we get

$$p_B^\circ = 550 \text{ mm of Hg} = \text{Vapour pressure of pure B}$$

$$p_A^\circ = 350 \text{ mm of Hg} = \text{Vapour pressure of pure A}$$

ILLUSTRATION 2.21

Mole fraction of component A in vapour phase is χ_1 and that of component A in liquid mixture is χ_2 ; then (p_A° = vapour pressure of pure A; p_B° = vapour pressure of pure B), the total vapour pressure of liquid mixture is

$$\text{a. } p_A^\circ \frac{\chi_2}{\chi_1} \quad \text{b. } p_A^\circ \frac{\chi_1}{\chi_2} \quad \text{c. } p_B^\circ \frac{\chi_1}{\chi_2} \quad \text{d. } p_B^\circ \frac{\chi_2}{\chi_1}$$

Sol.

$$\text{a. } p_A = p_A^\circ \chi_2, \text{ vapour pressure of A.}$$

$$\text{Mole fraction of A in vapour} = \frac{p_A}{p_{\text{total}}}$$

$$\chi_1 = \frac{p_A^\circ \chi_2}{P}$$

$$p_{\text{total}} = \frac{p_A^\circ \chi_2}{\chi_1}$$

ILLUSTRATION 2.22

Heptane and octane form an ideal solution. At 373 K, the vapour pressure of the two liquids are 105.0 kPa and 46.0 kPa, respectively. What will be the vapour pressure, of the mixture of 25 g of heptane and 35 g of octane?

$$\text{Sol. } Mw \text{ of heptane, } C_7H_{16}, Mw_A = 100$$

$$Mw \text{ of octane, } C_8H_{18}, Mw_B = 114$$

$$n_A = \frac{W_A}{Mw_A} = \frac{25}{100} = 0.25; \quad n_B = \frac{35}{114} = 0.3$$

$$\chi_A = \frac{0.25}{0.25 + 0.30}; \quad \chi_B = \frac{0.3}{0.25 + 0.30};$$

$$= 0.45 = 0.55$$

$$P = p_A^\circ \chi_A + p_B^\circ \chi_B$$

$$= 105.0 \times 0.45 + 46.0 \times 0.55$$

$$= 47.25 + 25.30$$

$$= 72.55 \text{ kPa}$$

ILLUSTRATION 2.23

Two liquids A and B form an ideal solution such that $p_A^\circ = 700 \text{ mm}$ and $p_B^\circ = 300 \text{ mm}$. A small amount of solution is vapourized and the vapour condensed (at equilibrium). The condensate has equilibrium vapour pressure of 500 mm (at same temperature). Find the composition of the original solution.

Sol.

$$P_t = P_A + P_B$$

$$P_t = p_A^\circ \chi_A + p_B^\circ \chi_B = 700\chi_A + 300(1 - \chi_A) \quad \dots(i)$$

$$= 300 + 400\chi_A$$

$$\chi_A^v = \frac{p_A}{P_t} = \frac{700\chi_A}{300 + 400\chi_A} = \frac{7\chi_A}{3 + 4\chi_A}$$

$$\chi_B^v = \frac{p_B}{P_t} = \frac{300\chi_B}{300 + 400\chi_A} = \frac{300(1 - \chi_A)}{300 + 400\chi_A} = \frac{3 - 3\chi_A}{3 + 4\chi_A}$$

Put value in Eq. (i)

$$500 = 700 \left(\frac{7\chi_A}{3 + 4\chi_A} \right) + 300 \left(\frac{3 - 3\chi_A}{3 + 4\chi_A} \right)$$

$$\therefore \chi_A = 0.3, \chi_B = 0.7$$

ILLUSTRATION 2.24

At 80°C, the vapour pressure of pure liquid A is 520 mm Hg and that of pure liquid B is 1000 mm Hg. If a mixture of solution A and B boils at 80°C and 1 atm pressure, the amount of A in the mixture is (1 atm = 760 mm Hg)

$$\text{a. 50 mol \%} \quad \text{b. 52 mol \%}$$

$$\text{c. 34 mol \%} \quad \text{d. 48 mol \%}$$

Sol.

$$\text{a. } P_M = p_A^\circ \chi_A + p_B^\circ \chi_B$$

$$P_M = p_A^\circ \chi_A + p_B^\circ (1 - \chi_A)$$

$$760 = 520\chi_A + 1000 - 1000\chi_A$$

$$\chi_A = \frac{240}{480} = 0.5$$

$$\text{Therefore, mol \%} = 50$$

ILLUSTRATION 2.25

At 298 K, the vapour pressure of pure liquid *n*-butane is 1823 torr and vapour pressure of pure liquid *n*-pentane is 521 torr and form nearly an ideal solution.

- Find the total vapour pressure at 298 K of a liquid solution containing 10% *n*-butane and 90% *n*-pentane by weight.
- Find the mole fraction of *n*-butane in solution exerting a total vapour pressure of 760 torr.
- What is composition of vapours of two components (mole fraction in vapour state)?

Sol.

$$P_{n\text{-butane}}^\circ = 1823 \text{ torr}; P_{n\text{-pentane}}^\circ = 521 \text{ torr}$$

- Given 10% *n*-butane by weight = 10 g
90% *n*-pentane by weight = 90 g

$$\therefore \text{moles of } n\text{-butane} = \frac{10}{58} \left(\begin{array}{l} Mw \text{ of } n\text{-butane} = 58 \\ Mw \text{ of } n\text{-pentane} = 72 \end{array} \right)$$

$$\text{moles of } n\text{-pentane} = \frac{90}{72}$$

$$\therefore \chi_{n\text{-butane}} = \frac{10/58}{10/58 + 90/72} = 0.122$$

$$\chi_{n\text{-pentane}} = 1 - \chi_{n\text{-butane}} = 1 - 0.122 = 0.878$$

From Raoult's law,

$$P_t = P_A^\circ \chi_A + P_B^\circ \chi_B = 0.122 \times 1823 + 0.878 \times 521$$

$$= 679.84 \text{ torr}$$

- Given $P_{\text{total}} = 760 \text{ torr}$; $P_{n\text{-butane}}^\circ = 1823 \text{ torr}$;
 $P_{n\text{-pentane}}^\circ = 521 \text{ torr}$

Let mole fraction of *n*-butane = y

mole fraction *n*-pentane = $1 - y$

Using Raoult's law, we have

$$P_t = P_A^\circ \chi_A + P_B^\circ \chi_B$$

$$760 = y(1823) + (1 - y)521$$

$$\therefore y = 0.183$$

c. The mole fraction in vapour state:

$$\chi_{n\text{-butane}}^v = \frac{P_{n\text{-butane}}}{P_{\text{total}}} = \frac{P_{n\text{-butane}}^\circ \times \chi_{n\text{-butane}}}{P_{\text{total}}} \\ = \frac{0.122 \times 1823}{679.84} = 0.327$$

$$\chi_{n\text{-pentane}}^v = \frac{P_{n\text{-pentane}}^\circ \times \chi_{n\text{-pentane}}}{P_{\text{total}}} \\ = \frac{521 \times 0.278}{679.84} = 0.673$$

χ^v is also called as vapour fraction.

ILLUSTRATION 2.26

The vapour pressure of pure water at 25°C is 23.00 torr. What is the vapour pressure of 100 g of water to which 100 g of $\text{C}_6\text{H}_{12}\text{O}_6$ (glucose) has been added?

Sol. Raoult's law: $P_{\text{solution}} = p_A = p_A^\circ \chi_A$

$$\Rightarrow P_{\text{solution}} = p_A^\circ \frac{n_A}{n_A + n_B} = p_A^\circ \frac{\frac{W_A}{Mw_A}}{\frac{W_A}{Mw_A} + \frac{W_B}{Mw_B}}$$

$$\Rightarrow = 23.00 \times \frac{\frac{100}{18}}{\frac{100}{18} + \frac{100}{180}}$$

$$[Mw_{\text{Glucose}} = 180 \text{ g mol}^{-1}; p_A^\circ = 23.0 \text{ torr}]$$

$$\Rightarrow P_{\text{solution}} = 21.294 \text{ torr}$$

ILLUSTRATION 2.27

4.375 g of a substance when dissolved in 36.0 g of water, lowered its vapour pressure by 0.5 mm at a given temperature. The vapour pressure of water at this temperature is 25.0 mm. Calculate the molecular weight of solute.

Sol. $\Delta P = 0.5$ mm, using the formula for lowering of vapour pressure:

$$\frac{\Delta P}{P_A^\circ} = \chi_B = \frac{n_B}{n_A + n_B} = \frac{W_B/Mw_B}{W_A/Mw_A + W_B/Mw_B}$$

$$\Rightarrow \frac{0.5}{25} = \frac{4.375/Mw_B}{36/18 + 4.375/Mw_B}$$

$$\Rightarrow Mw_B = 109.38 \text{ g mol}^{-1}$$

ILLUSTRATION 2.28

Assuming ideal behaviour, calculate the pressure of 1.0 molal solution of a non-volatile molecular solute in water at 50°C. The vapour pressure of water at 50°C is 0.222 atm.

Sol. $P_{\text{solution}} = P_A = P_A^\circ \chi_A$ (Raoult's law)

By using the relation between molality and mole fraction, we have;

$$m = \frac{\chi_B}{\chi_A} \times \frac{1000}{Mw_A} = \frac{1 - \chi_A}{\chi_A} \times \frac{1000}{Mw_A}$$

$$\Rightarrow \chi_A = \frac{1000}{mMw_A + 1000} \\ = \frac{1000}{1 \times 18 + 1000} = \frac{1000}{1018} = 0.982$$

$$\Rightarrow P_{\text{solution}} = P_A^\circ \chi_A = 0.222 \times 0.982 = 0.218 \text{ atm}$$

ILLUSTRATION 2.29

At a certain temperature, the vapour pressure of pure ether is 640 mm and that of pure acetone is 280 mm. Calculate the mole fraction of each component in the vapour state if the mole fraction of ether in the solution is 0.50.

Sol. In the given solution, both ether and acetone are volatile, so from Raoult's law, we can have vapour pressure of solution (P_{total}).

$$\text{Note: } \chi_{A(\text{Liquid phase})} = \frac{p_A}{p_A^\circ}, \chi_{A(\text{Vapour phase})} = \frac{p_A}{p_A + p_B}$$

Let A is ether and B is acetone.

$$P_{\text{total}} = p_A + p_B = p_A^\circ \chi_A + p_B^\circ \chi_B \\ = 640 \times 0.5 + 280 \times 0.5 = 460.0 \text{ mm}$$

Now mole fraction in vapour state is given as follows:

$$\chi_{A(\text{vapour})} = \frac{p_A}{P_{\text{total}}} = \frac{p_A^\circ \chi_A}{P_{\text{total}}} = \frac{640 \times 0.5}{460.0} = 0.6956$$

$$\chi_{B(\text{vapour})} = \frac{p_B}{P_{\text{total}}} = \frac{p_B^\circ \chi_B}{P_{\text{total}}} = \frac{280 \times 0.5}{460.0} = 0.304$$

ILLUSTRATION 2.30

The vapour pressure of methyl alcohol at 298 K is 0.158 bar. The vapour pressure of this liquid in solution with liquid B is 0.095 bar. Calculate the mole fraction of methyl alcohol in the solution if the mixture obeys Raoult's law.

Sol. Given $P_{\text{methyl alcohol}}^\circ = 0.158$ bar

$$P_{\text{solution}} = 0.095 \text{ bar}$$

According to Raoult's law

$$P = \chi_1 P^\circ \quad (\chi_1 = \text{mole fraction of methyl alcohol})$$

$$\therefore 0.095 = \chi_1 \times 0.158$$

$$\chi_1 (\text{mole fraction of methyl alcohol}) = \frac{0.095}{0.158} = 0.601$$

ILLUSTRATION 2.31

The vapour pressure of acetone at 298 K is 40 mm of Hg. Its mole fraction in a solution with alcohol is 0.80. What is its vapour pressure in solution if the mixture obey Raoult's law?

Sol. The given values are

$$P_{\text{acetone}}^\circ = 40 \text{ mm of Hg}$$

$$\chi_{\text{acetone}} = 0.80$$

According to Raoult's law

$$P_A = P_A^\circ \chi_A$$

On substituting all values, we get

$$\text{Vapour pressure of acetone in solution} = 40 \times 0.80 \\ = 32 \text{ mm of Hg}$$

ILLUSTRATION 2.32

100 g of water contains 1.0 g urea and 2.0 g sucrose at 298 K. The vapour pressure of water at 298 K is 0.3 atm. Calculate the vapour pressure of the solution. (Molecular weight of urea = 60; Molecular weight of sucrose = 342)

Sol. The given values are

$$\begin{aligned} W_{\text{H}_2\text{O}} &= 100 \text{ g} & ; & & M_{w_{\text{H}_2\text{O}}} &= 18 \text{ g mol}^{-1} \\ W_{\text{urea}} &= 1.0 \text{ g} & ; & & M_{w_{\text{urea}}} &= 60 \text{ g mol}^{-1} \\ W_{\text{sucrose}} &= 2.0 \text{ g} & ; & & M_{w_{\text{sucrose}}} &= 342 \text{ g mol}^{-1} \\ P_{\text{H}_2\text{O}}^\circ &= 0.3 \text{ atm} \end{aligned}$$

Amount fraction of solvent

$$\begin{aligned} &= \frac{\text{Amount of solvent}}{\text{Amount of (solvent + solute)}} \\ &= \frac{100/18}{(100/18 + 1/60 + 2/342)} \\ &= \frac{5.556}{5.577} = 0.99 \end{aligned}$$

According to Raoult's law,

$$p_A = p_A^\circ \chi_A$$

$$\therefore \text{Vapour pressure of solution} = 0.3 \times 0.99 = 0.29 \text{ atm}$$

ILLUSTRATION 2.33

Benzene and toluene form nearly ideal solution. At 298 K, the vapour pressure of pure benzene is 150 torr and of pure toluene is 50 torr. Calculate the vapour pressure of the solution, containing equal weights of two substances at this temperature?

Sol. Let the weights of benzene and toluene in the solution is = W g

$$\text{Mole fraction of benzene, } \chi_b = \frac{\frac{W}{78}}{\frac{W}{78} + \frac{W}{92}} = 0.541$$

$$\text{Mole fraction of toluene } \chi_t = 1 - 0.541 = 0.459$$

According to Raoult's law $p_A = p_A^\circ \chi_A$

$$\therefore \text{Partial pressure of benzene, } p_b = p_b^\circ \times \chi_b = 150 \times 0.541 = 81.15 \text{ torr}$$

$$\therefore \text{Partial pressure of toluene, } p_t = p_t^\circ \times \chi_t = 50 \times 0.459 = 22.95 \text{ torr}$$

$$\begin{aligned} \text{Total vapour pressure of solution} &= p_b + p_t \\ &= 81.15 + 22.95 \\ &= 104.1 \text{ torr} \end{aligned}$$

ILLUSTRATION 2.34

At 20°C, the vapour pressure of pure liquid A is 22 mm Hg and that of pure liquid B is 75 mm Hg. What is the composition of the solution of these two components that has vapour pressure of 48.5 mm Hg at this temperature?

Sol. The given values are

$$p_A^\circ = 22 \text{ mm Hg}; p_B^\circ = 75 \text{ mm Hg}; P_{\text{total}} = 48.5 \text{ mm Hg}$$

Let χ_A and χ_B are the mole fractions of liquids A and B, respectively, in solution, then

$$p_A = p_A^\circ \chi_A = 22 \chi_A$$

$$p_B = p_B^\circ \chi_B = p_B^\circ (1 - \chi_A) = 75 (1 - \chi_A)$$

$$P_{\text{total}} = p_A + p_B = 22\chi_A + 75(1 - \chi_A) = 48.5$$

$$\therefore \chi_A = 0.5 \text{ and } \chi_B = 1 - \chi_A = 0.5$$

ILLUSTRATION 2.35

An aqueous solution containing 28% by weight of a liquid A (molecular mass = 140) has a vapour pressure of 0.200 bar at 37°C. Calculate the vapour pressure of pure liquid (vapour pressure of water at 37°C = 0.100 bar).

Sol. The given values are:

$$W_{\text{liquid}} = 28 \text{ g}, M_{w_l} = 140$$

$$W_{\text{H}_2\text{O}} = 72 \text{ g}; M_{w_{\text{H}_2\text{O}}} = 18$$

$$p_{\text{H}_2\text{O}}^\circ = 0.10 \text{ bar}; P_{\text{total}} = 0.2 \text{ bar}$$

$$\text{Mole fraction of liquid, } \chi_l = \frac{\frac{28}{140}}{\frac{28}{140} + \frac{72}{18}} = 0.048$$

$$\text{Mole fraction of water, } \chi_{\text{H}_2\text{O}} = 1 - 0.048 = 0.952$$

According to Raoult's law

$$P_{\text{total}} = p_l^\circ \chi_l + p_{\text{H}_2\text{O}}^\circ \chi_{\text{H}_2\text{O}}$$

$$0.2 = p_l^\circ \times 0.048 + 0.1 \times 0.952$$

$$\text{or } p_l^\circ = \frac{0.2 - 0.1 \times 0.952}{0.048} = 2.18 \text{ bar}$$

Therefore, the vapour pressure of pure liquid is 2.18 bar.

ILLUSTRATION 2.36

Two liquids A and B have vapour pressure of 0.600 bar and 0.2 bar, respectively. In an ideal solution of the two, calculate the mole fraction of A at which the two liquids have equal partial pressures.

Sol. Let the mole fraction of A = χ

$$\text{Mole fraction of B} = 1 - \chi$$

$$\text{Partial pressure of A} = 0.6\chi$$

$$\text{Partial pressure of B} = 0.2(1 - \chi)$$

$$\text{or } 0.6\chi = 0.2(1 - \chi)$$

$$\chi = 0.25$$

Hence, the mole fraction of A = 0.25.

ILLUSTRATION 2.37

Two liquids A and B have vapour pressures in the ratio of $p_A^\circ : p_B^\circ = 1 : 2$ at a certain temperature. Suppose we have an ideal solution of A and B in the mole fraction ratio A : B = 1 : 2. What would be the mole fraction of A in the vapour in equilibrium with the solution at a given temperature?

a. 0.25

b. 0.2

c. 0.5

d. 0.33

Sol.

b. $p_A^\circ : p_B^\circ = 1 : 2$

$$p_A = \chi_A \times p_A^\circ = A \times \chi_A$$

$$p_B = \chi_B \times p_B^\circ = 2A \times 2\chi_A$$

$$P_{\text{total}} = A\chi_A + 4A\chi_A = 5A\chi_A$$

$$\chi_{A(\text{vapour phase})} = \frac{p_A}{P_{\text{total}}} = \frac{A\chi_A}{5A\chi_A} = \frac{1}{5} = 0.2$$

ILLUSTRATION 2.38

A certain ideal solution of two liquids A and B has mole fraction of 0.3 and 0.5 for the vapour phase and liquid phase, respectively. What would be the mole fraction of B in the vapour phase, when the mole fraction of A in the liquid is 0.25?

Sol. $\chi_A(\text{vap}) = 0.3$, $\chi_B(\text{liq}) = 0.5$, $\chi_A(\text{liq}) = 0.5$

$$p_A = \chi_A p_A^\circ = 0.5 p_A^\circ; p_B = \chi_B p_B^\circ = 0.5 p_B^\circ$$

$$P_{\text{total}} = p_A + p_B = 0.5 p_A^\circ + 0.5 p_B^\circ = 0.5 (p_A^\circ + p_B^\circ)$$

$$\chi_A(\text{vap}) = \frac{p_A}{P_{\text{total}}}$$

$$0.3 = \frac{0.5 p_A^\circ}{0.5 (p_A^\circ + p_B^\circ)} = 0.3 = \frac{p_A^\circ}{p_A^\circ + p_B^\circ}$$

On rewriting it,

$$\frac{1}{0.3} = \frac{p_A^\circ + p_B^\circ}{p_A^\circ} = 1 + \frac{p_B^\circ}{p_A^\circ}$$

$$\Rightarrow \frac{p_B^\circ}{p_A^\circ} = \frac{1}{0.3} - 1 = \frac{0.7}{0.3} = \frac{7}{3}$$

$$\therefore \frac{p_A^\circ}{p_B^\circ} = \frac{0.3}{0.7} = \frac{3}{7} \Rightarrow p_A^\circ = \frac{3}{7} p_B^\circ$$

$$\chi_A(\text{liq}) = 0.25, \chi_B(\text{liq}) = 0.75$$

$$p_A = 0.25 p_A^\circ = 0.25 \times \frac{3}{7} p_B^\circ$$

$$p_B = 0.75 p_B^\circ$$

$$\begin{aligned} \therefore P_{\text{total}} = p_A + p_B &= 0.25 \times \frac{3}{7} p_B^\circ + 0.75 p_B^\circ \\ &= 0.75 \times \frac{8}{7} p_B^\circ \end{aligned}$$

$$\chi_B(\text{vap}) = \frac{p_B}{P_{\text{total}}} = \frac{0.75 p_B^\circ}{0.75 \times \frac{8}{7} p_B^\circ} = \frac{7}{8}$$

$$0.45 = \frac{0.65 \times p_x^\circ}{400}$$

$$\therefore p_x^\circ = 276.9 \text{ mm}$$

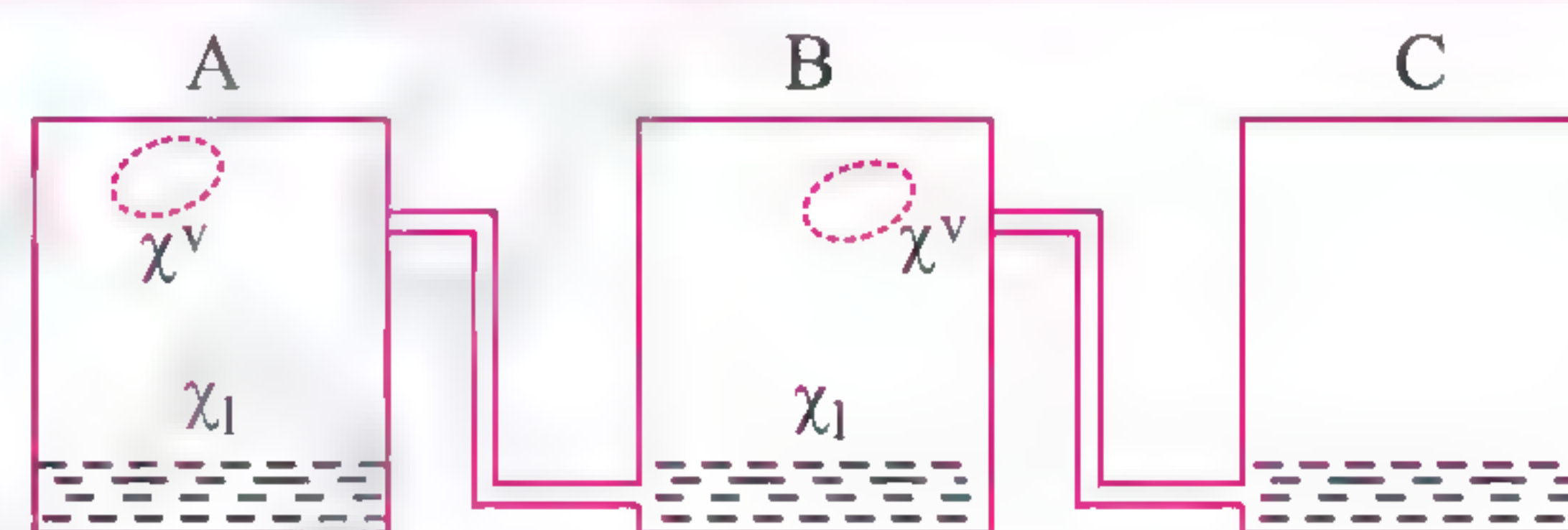
$$0.65 \times 276.9 + 0.35 p_y^\circ = 400$$

$$p_y^\circ = 628.6 \text{ mm}$$

ILLUSTRATION 2.40

Liquids X and Y form an ideal solution. The vapour pressure of X and Y at 100°C are 300 and 100 mm of Hg, respectively. Suppose that a solution composed of 1 mol of X and 1 mol of Y at 100°C is collected and condensed. This condensate is then heated at 100°C and vapour is again condensed to form a liquid A. What is the mole fraction of X in A?

Sol.



In vessel A

$$p_X^\circ = 300, p_Y^\circ = 100 \text{ mm}$$

$$\chi_X = \frac{1}{2}, \quad \chi_Y = \frac{1}{2}$$

$$p_X = 300 \times \frac{1}{2} = 150,$$

$$p_Y = 100 \times \frac{1}{2} = 50$$

$$\chi_X^v = \frac{150}{200} = \frac{3}{4}$$

$$\chi_Y^v = 1 - \frac{3}{4} = \frac{1}{4}$$

In vessel B

$$\chi_X \text{ in B} = \frac{3}{4}$$

$$\chi_Y \text{ in B} = \frac{1}{4}$$

$$p_X = \chi_X \times p_X^\circ$$

$$p_X = \frac{3}{4} \times 300 = 225$$

$$p_Y = \chi_Y \times p_Y^\circ$$

$$p_Y = \frac{1}{4} \times 100 = 25$$

$$p_X + p_Y = 225 + 25 = 250$$

$$\chi_X^v \text{ in B} = \frac{225}{250} = 0.9 \quad \left(\because \begin{array}{cc} \chi_X(\text{liquid}) &= \chi_X^v \text{ in B} \\ \text{in C Vessel} & \text{Vessel} \end{array} \right)$$

ILLUSTRATION 2.39

Solution of two volatile liquids x and y obey Raoult's law. At a certain temperature it is found that when the total pressure above a given solution is 400 mm of Hg, the mole fraction of x in the vapour is 0.45 and in the liquid is 0.65. What are the vapour pressures of two pure liquids at the given temperature?

Sol. $\chi_x \text{ in liquid} = 0.65$

$$\chi_y \text{ in liquid} = 0.35$$

$$p_x = \chi_x p_x^\circ$$

$$p_y = \chi_y p_y^\circ \quad p_y = 0.35 p_y^\circ \quad p_x = 0.65 p_x^\circ$$

$$P_{\text{total}} = p_x + p_y = 400$$

$$\chi_x^v = 0.45 = \frac{p_x}{P_{\text{total}}}$$

ILLUSTRATION 2.41

A liquid mixture of benzene and toluene is composed of 1 mol of benzene and 1 mol of toluene.

- If the pressure over the mixture at 300 K is reduced, at what pressure does the first vapour form?
- What is the composition of the first trace of vapour formed?
- If the pressure is reduced further, at what pressure does the last trace of liquid disappear?
- What is the composition of the last trace of liquid?
- What will be the pressure, the composition of the liquid, and the composition of the vapour, when 1 mol of the mixture is vapourized?

Given: $p_T^\circ = 32.05$ mm Hg, $p_B^\circ = 103$ mm Hg

Sol.

- The first vapour will be formed when the external pressure becomes equal to the vapour pressure of the system.

$$P = \chi_T p_T^\circ + p_B^\circ \chi_B$$

$$P = \frac{1}{2}(32.05) + \frac{1}{2}(103) = 67.52 \text{ mm Hg}$$

- Composition of the first trace of vapour formed

$$\chi_T = \frac{P_T^\circ \chi_T}{P} = \frac{0.5 \times 32.05}{67.52} = 0.24$$

$$\chi_B = 1 - 0.24 = 0.76$$

- The last trace of liquid will disappear when the composition of the vapour phase become $\chi_B = 0.5$ and $\chi_T = 0.5$. The pressure at which this occurs can be calculated as

$$\frac{1}{P} = \frac{\chi_T}{P_T^\circ} + \frac{\chi_B}{P_B^\circ} = \frac{0.5}{32.05} + \frac{0.5}{103}$$

$$P = 49.01 \text{ mm Hg}$$

- Composition of the last trace of the liquid will be

$$\chi_B = \frac{P_B^\circ \chi_B}{P}$$

$$0.5 = \frac{32.05 \chi_B}{49.01}$$

$$\chi_B = 0.76 \text{ and } \chi_T = 0.24$$

- $\chi_T = 0.642$, $\chi_B = 0.358$ and

$$\chi_B = 0.642, \chi_T = 0.358, P = 57.46 \text{ mm Hg}$$

ILLUSTRATION 2.42

Ethylene bromide $\text{C}_2\text{H}_4\text{Br}_2$, and 1,2-dibromopropane, $\text{C}_3\text{H}_6\text{Br}_2$, form a series of ideal solutions over the whole range of composition. At 85°C , the vapour pressure of these two pure liquids are 173 and 127 torr, respectively.

- If 10.0 g of ethylene bromide is dissolved in 80.0 g of 1,2-dibromopropane, calculate the partial pressure of each component and the total pressure of the solution at 85°C .
- Calculate the mole fraction of ethylene bromide in the vapour in equilibrium with the above solution.
- What would be the mole fraction of ethylene bromide in a solution at 85°C equilibrated with a 50 : 50 mole mixture in the vapour?

Sol.

- Moles of $\text{C}_2\text{H}_4\text{Br}_2 = 10/188 = 0.0532$

$$\text{Moles of } \text{C}_3\text{H}_6\text{Br}_2 = 80/202 = 0.396$$

$$\chi_{(\text{C}_2\text{H}_4\text{Br}_2)} = \frac{0.0532}{0.0532 + 0.396} = 0.118$$

$$P_{(\text{C}_2\text{H}_4\text{Br}_2)} = p^\circ \chi_{(\text{C}_2\text{H}_4\text{Br}_2)} = 173 \text{ torr} \times 0.118 = 20.4 \text{ torr}$$

$$P_{(\text{C}_3\text{H}_6\text{Br}_2)} = p^\circ \chi_{(\text{C}_3\text{H}_6\text{Br}_2)} = 127 \text{ torr} \times 0.882 = 112 \text{ torr}$$

$$P_{\text{total}} = 20.4 + 112 = 132.4$$

- $\chi_{(\text{C}_2\text{H}_4\text{Br}_2)}^v = \frac{P_{(\text{C}_2\text{H}_4\text{Br}_2)}}{P_{\text{total}}} = 20.4/132.4 = 0.155$

$$\begin{aligned} P_{(\text{C}_2\text{H}_4\text{Br}_2)} &= P_{(\text{C}_3\text{H}_6\text{Br}_2)} \\ 173 \chi_{(\text{C}_2\text{H}_4\text{Br}_2)} &= 127 \chi_{(\text{C}_3\text{H}_6\text{Br}_2)} \\ &= 127 (1 - \chi_{\text{C}_3\text{H}_6\text{Br}_2}) \end{aligned}$$

$$173 \chi = 127 (1 - \chi)$$

$$300 \chi = 127 \Rightarrow \chi = 0.423.$$

ILLUSTRATION 2.43

The vapour pressures of two pure liquids A and B that form an ideal solution are 300 and 800 torr, respectively, at temperature T . A mixture of the vapours of A and B for which the mole fraction of A is 0.25 is slowly compressed at temperature T . Calculate

- The composition of the first drop of the condensate.
- The total pressure when this drop is formed.
- The composition of the solution whose normal boiling point is T .
- The pressure when only the last bubble of vapour remains.
- Composition of the last bubble.

Sol.

Given

$$p_A^\circ = 300 \text{ torr},$$

$$\chi_A^l = 0.25, \chi_B^l = 1 - 0.25 = 0.75$$

- By the condensation of only one drop, we can assume that the composition of the vapour remains the same.

$$\chi_A^v = \frac{p_A^\circ \chi_A^l}{P_T} \text{ and } \chi_B^v = \frac{p_B^\circ \chi_B^l}{P_T}$$

$$\text{or } \frac{\chi_A^v}{\chi_B^v} = \frac{p_A^\circ \chi_A^l}{p_B^\circ (1 - \chi_A^l)}$$

Putting various known values, we get

$$\chi_A^v = 0.111 \text{ and } \chi_B^v = 0.888$$

- $P = p_A^\circ \chi_A^v + p_B^\circ \chi_B^v$

$$= 300 \times 0.11 + 800 \times 0.888$$

$$= 743.7$$

- $760 = 300 \chi_A + 800 \chi_B$

$$\chi_A = 0.08 \text{ and } \chi_B = 0.92$$

- When only the last bubble of vapour remains, we can assume the composition of vapour is now the composition of the condensate.

$$\text{Hence, } P = 0.25 \times 300 + 0.75 \times 800 = 675 \text{ torr}$$

e. Composition of last bubble

$$\chi_A = \frac{p_A^\circ \chi_A}{P} = \frac{0.25 \times 300}{675} = 0.11$$

$$\chi_B = 0.89$$

ILLUSTRATION 2.44

Calculate the vapour pressure lowering of a 0.1 m aqueous solution of non-electrolyte at 75°C.

$$\Delta H = 9.720 \text{ kcal mol}^{-1}, P_2 = 742.96 \text{ torr}$$

Sol. The vapour pressure of pure water, P_A° , at 75°C is

$$\begin{aligned} \log \frac{P_2}{P_1} &= \frac{\Delta H^\circ}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \\ &= \frac{9720}{2.30 \times 1.978} \left(\frac{1}{348} - \frac{1}{373} \right) = 0.410 \end{aligned}$$

$$\frac{P_2}{P_1} = 2.51; P_1 = 296 \text{ torr}$$

The vapour pressure lowering due to 0.100 m solute is

$$\Delta P = \frac{mMw_A P_A^\circ}{1000} = \frac{0.1 \times 18 \times 296}{1000} = 0.533$$

ILLUSTRATION 2.45

What is the composition of the vapour which is in equilibrium at 30°C with a benzene–toluene solution with a mole fraction of benzene of (a) 0.400 and (b) 0.600?

$$p_b^\circ = 119 \text{ torr}, p_t^\circ = 37.0 \text{ torr}$$

Sol. $p_b = 0.400 \times 119 \text{ torr} = 47.6 \text{ torr}$

$$p_t = 0.600 \times 37.0 \text{ torr} = 22.2 \text{ torr}$$

$$p_{\text{total}} = (47.6 + 22.2) = 69.8 \text{ torr}$$

The composition of vapour is determined by applying Dalton's law of partial pressures:

$$\chi_b = \frac{p_b}{P_{\text{total}}} = \frac{47.6}{69.8} = 0.682$$

$$\chi_b = \frac{22.2}{69.8} = 0.318 = 1.000 - 0.682$$

Similarly, for the case of the solution in which the mole fraction of toluene is 0.400,

$$\chi_b = \frac{71.5}{86.3} = 0.829, \chi_t = \frac{14.8}{86.3} = 0.171$$

ILLUSTRATION 2.46

Two liquids A and B form an ideal solution at temperature T . When the total vapour pressure above the solution is 600 torr, the amount fraction of A in the vapour phase is 0.40 and in the liquid phase is 0.60. What are the vapour pressures of pure A and pure B at temperature T ?

Sol. The given data are

$$\chi_A = 0.60; \chi_A^V = 0.40; P_t = 600 \text{ torr}$$

$$p_A^\circ = ?, p_B^\circ = ?$$

Using equation $\chi_i^V = p_i/P_{\text{total}}$

$$\chi_A^V = \frac{p_A}{P} = \frac{\chi_A p_A^\circ}{P}$$

$$\text{or } p_A^\circ = \frac{\chi_A^V P}{\chi_A} = \frac{(0.40)(600)}{(0.60)} = 400 \text{ torr}$$

$$\text{Similarly, } p_B^\circ = \frac{\chi_B^V P}{\chi_B} = \frac{(0.60)(600)}{(0.40)} = 900 \text{ torr}$$

ILLUSTRATION 2.47

The vapour pressure of chloroform (CHCl_3) and dichloromethane (CH_2Cl_2) at 298 K is 200 mm Hg and 415 mm Hg, respectively. Calculate

(a) The vapour pressure of the solution prepared by mixing 25.5 g of CHCl_3 and 40 g of CH_2Cl_2 at 298 K.

(b) Mole fractions of each component in vapour phase.

Sol. (a) Molar mass of $\text{CH}_2\text{Cl}_2 = 12 \times 1 + 1 \times 2 + 35.5 \times 2 = 85 \text{ g mol}^{-1}$

$$\begin{aligned} \text{Molar mass of } \text{CHCl}_3 &= 12 \times 1 + 1 \times 1 + 35.5 \times 3 \\ &= 119.5 \text{ g mol}^{-1} \end{aligned}$$

$$\text{Moles of } \text{CH}_2\text{Cl}_2 = \frac{40 \text{ g}}{85 \text{ g mol}^{-1}} = 0.47 \text{ mol}$$

$$\text{Moles of } \text{CHCl}_3 = \frac{25.5 \text{ g}}{119.5 \text{ g mol}^{-1}} = 0.213 \text{ mol}$$

$$\text{Total number of moles} = 0.47 + 0.213 = 0.683 \text{ mol}$$

$$\chi_{\text{CH}_2\text{Cl}_2} = \frac{0.47 \text{ mol}}{0.683 \text{ mol}} = 0.688$$

$$\chi_{\text{CHCl}_3} = 1.00 - 0.688 = 0.312$$

$$\begin{aligned} P_{\text{total}} &= p_{\text{CHCl}_3}^\circ + (p_{\text{CH}_2\text{Cl}_2}^\circ - p_{\text{CHCl}_3}^\circ) \chi_{\text{CH}_2\text{Cl}_2} \\ &= 200 + (415 - 200) \times 0.688 \\ &= 347.9 \text{ mm Hg} \end{aligned}$$

(b) To calculate the mole fraction of component in vapour phase,

$$\chi_i^V = \frac{p_i}{P_T}$$

$$\therefore p_{\text{CH}_2\text{Cl}_2} = 0.688 \times 415 \text{ mm Hg} = 285.5 \text{ mm Hg}$$

$$p_{\text{CHCl}_3} = 0.312 \times 200 \text{ mm Hg} = 62.4 \text{ mm Hg}$$

$$\chi_{\text{CH}_2\text{Cl}_2}^V = \frac{285.5}{347.9} = 0.82$$

$$\chi_{\text{CHCl}_3}^V = \frac{62.4}{347.9} = 0.18$$

Note: Since CH_2Cl_2 is a more volatile component than CHCl_3 [$p_{\text{CH}_2\text{Cl}_2}^\circ = 415 \text{ mm Hg}$ and $p_{\text{CHCl}_3}^\circ = 200 \text{ mm Hg}$] and the vapour phase is also richer in CH_2Cl_2 [$\chi_{\text{CH}_2\text{Cl}_2}^V = 0.82$ and $\chi_{\text{CHCl}_3}^V = 0.18$], it may be concluded that at equilibrium, vapour phase will be always rich in the component which is more volatile.

CONCEPT APPLICATION EXERCISE 2.1

- At same temperature, the vapour pressure of pure benzene, is 0.20 bar and the vapour pressure of pure toluene is 0.09 bar. If the mole fraction of toluene in a solution is 0.60
 - What is the total vapour pressure of the solution?
 - Calculate the composition of the vapour in terms of mole fraction.
- At 20°C, the vapour pressure of pure liquid A is 22 mm Hg and that of pure liquid B is 75 mm Hg. What is the composition of the solution of these two components that has a vapour pressure of 48.5 mm Hg at this temperature (assume ideal behaviour)?
- Pressure of 0.210 bar at 37°C. Calculate the vapour pressure of pure liquid (vapour pressure of water at 37°C = 0.198 bar).

ANSWERS

- a. $P_t = 0.134$ bar b. $\chi_{\text{benzene}}^V = 0.597$; $\chi_{\text{toluene}}^V = 0.402$
- $\chi_A = 0.5 = \chi_B$ 3. $P_t^\circ = 0.448$ bar

2.9 AZEOTROPIC MIXTURES

Binary mixtures that have same composition in liquid and vapour phase and boil at a constant temperature and can distil unchanged in composition are known as azeotropic mixtures or simply azeotropes (Greek meaning boiling without change). Thus, azeotropes behave as pure liquids.

There are two types of azeotropes called as minimum boiling azeotropes and maximum boiling azeotropes respectively.

(a) Minimum boiling azeotropes: The non-ideal binary solutions which show a very large positive deviation from Raoult's law form minimum boiling azeotropes at a constant composition. For example, the solution of ethanol–water shows a large positive deviation from Raoult's law (Fig. 2.12) as we can see from vapours-pressure–composition graph. A solution at a particular composition has a higher vapour

pressure and a lower boiler point than for any one of its pure components. At this point the composition of liquid and vapour phases is same and the liquid boils at a constant temperature which is lower than the boiling temperature of either of the pure component (Fig. 2.13, temperature–composition graph).

We indicate the composition of the vapour phase by upper curve and composition of the liquid phase by lower curve. At the boiling point temperature ($T^V = 351$ K), the composition of an azeotrope is $\chi_{(\text{H}_2\text{O})} = 0.056$ and $\chi_{(\text{C}_2\text{H}_5\text{OH})} = 0.944$, while the boiling point of pure ethanol and water is 351.5 K and 373 K, respectively, which are higher than the boiling point of azeotrope. (Table 2.3)

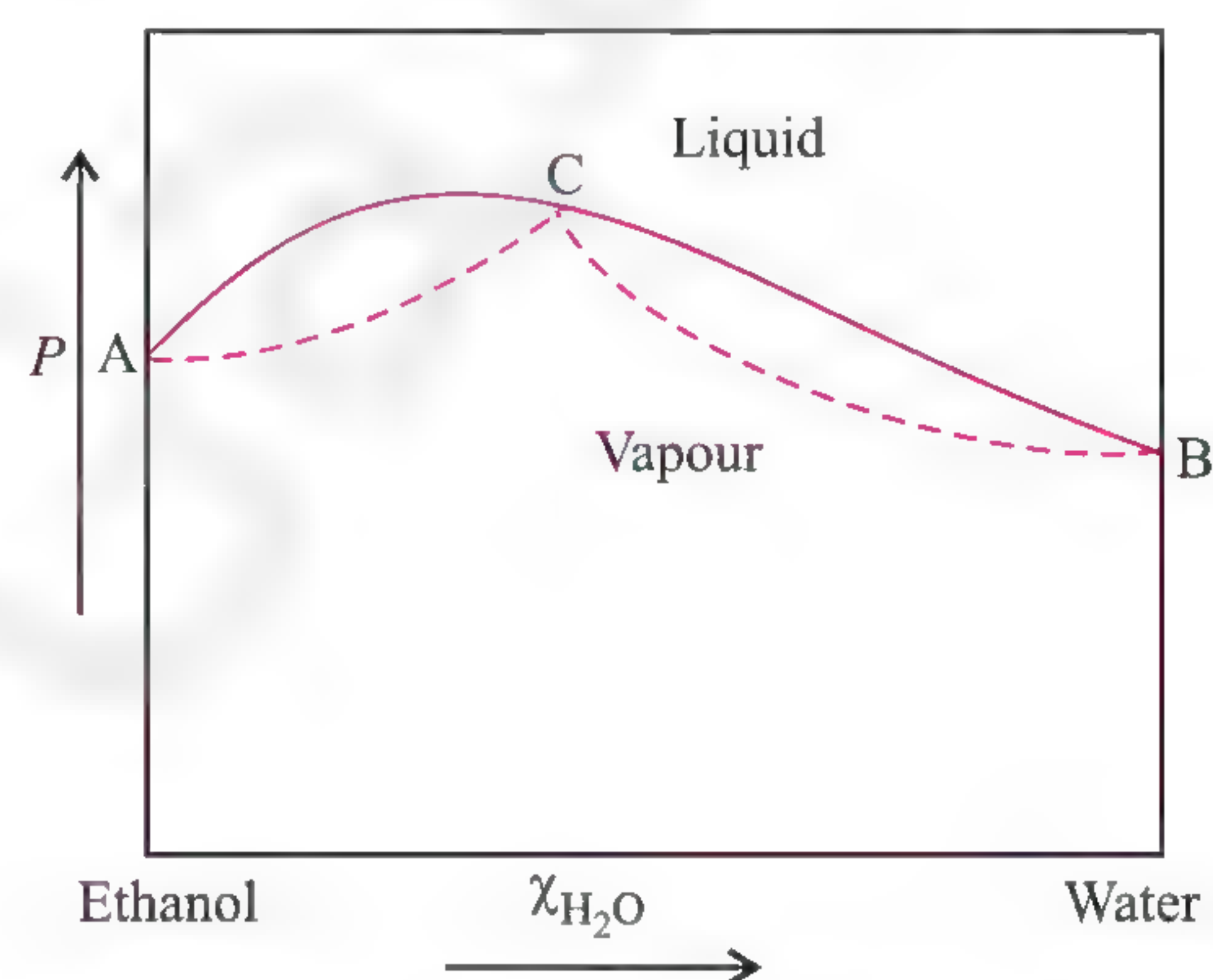


Fig. 2.12 Vapour pressure–composition graph

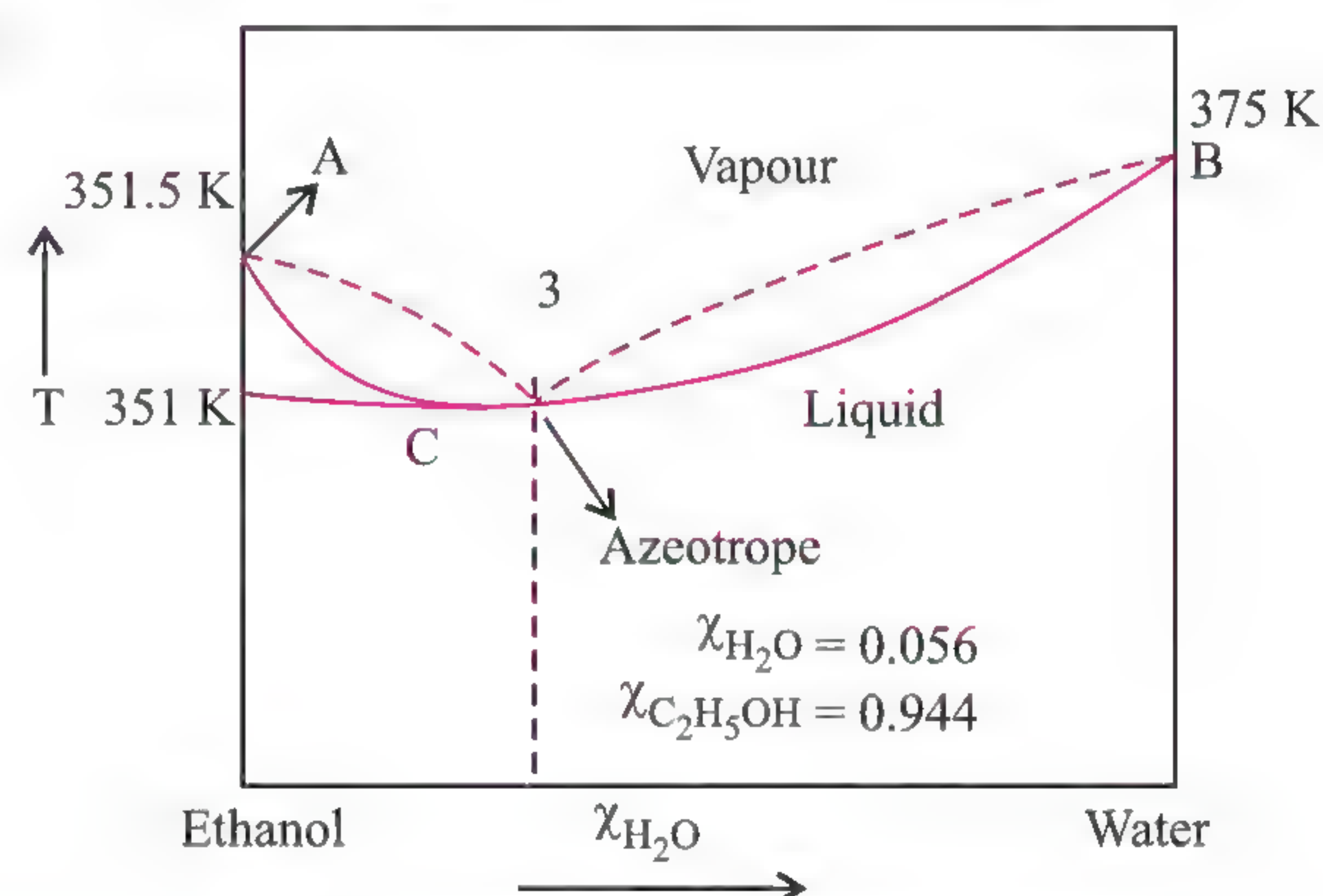


Fig. 2.13 Temperature–composition graph

Table 2.3 Some azeotropic mixtures

Components		Composition by weight % of B	Boiling point		
A	B		A	B	Azeotrope
Minimum boiling azeotropes (positive deviations)					
H ₂ O	C ₂ H ₅ OH	95.57	373.00	351.5	351.15
H ₂ O	C ₃ H ₇ OH	71.69	373.00	370.19	350.72
(CH ₃) ₂ CO	CS ₂	67	329.25	319.25	312.25
CHCl ₃	C ₂ H ₅ OH	6.8	334.2	351.3	332.3
Maximum boiling azeotropes (negative deviations)					
H ₂ O	HCl	20.3	373.0	188	383
H ₂ O	HI	57.0	373.0	239	400
H ₂ O	HNO ₃	68.0	373.0	359	393.5
H ₂ O	HClO ₄	71.6	373.0	383	476
H ₂ O	H ₂ SO ₄	98.3%	373.0	—	611

The fractional distillation of solution will only give any one of the pure components (A or B) and azeotropic mixture c. The fractional distillation is able to concentrate the alcohol to its best, the azeotropic composition of approximately 95% by volume of ethanol. Once the composition has been obtained the liquid and vapour have the same composition and therefore, it cannot be further distilled to separate water, from ethanol. Other methods of separation have to be used for preparing 100% ethanol.

(b) Maximum boiling azeotropes: The non-ideal solution which shows negative deviation from Raoult's law form maximum boiling azeotropes. From the vapour-pressure–composition diagram (Fig. 2.14), we can see that the solution has a minimum vapour pressure at a particular composition. This leads to a maximum on the boiling-point–composition diagram (Fig. 2.15). At this composition the solution boils at constant temperature without a change in the composition, i.e., the liquid phase and vapour phase have same composition. For example, a solution of HNO_3 and H_2O forms a maximum boiling point azeotropes. The composition of this azeotrope is 68% nitric acid and 32% water by mass and the boiling point is 393 K (Table 2.4).

(c) Preparation of absolute alcohol: Absolute alcohol is prepared by azeotropic distillation method. Rectified spirit (95% $\text{C}_2\text{H}_5\text{OH}$) is mixed with a suitable amount of benzene and subjected to fractional distillation. The fractions obtained are shown in Table 2.4.

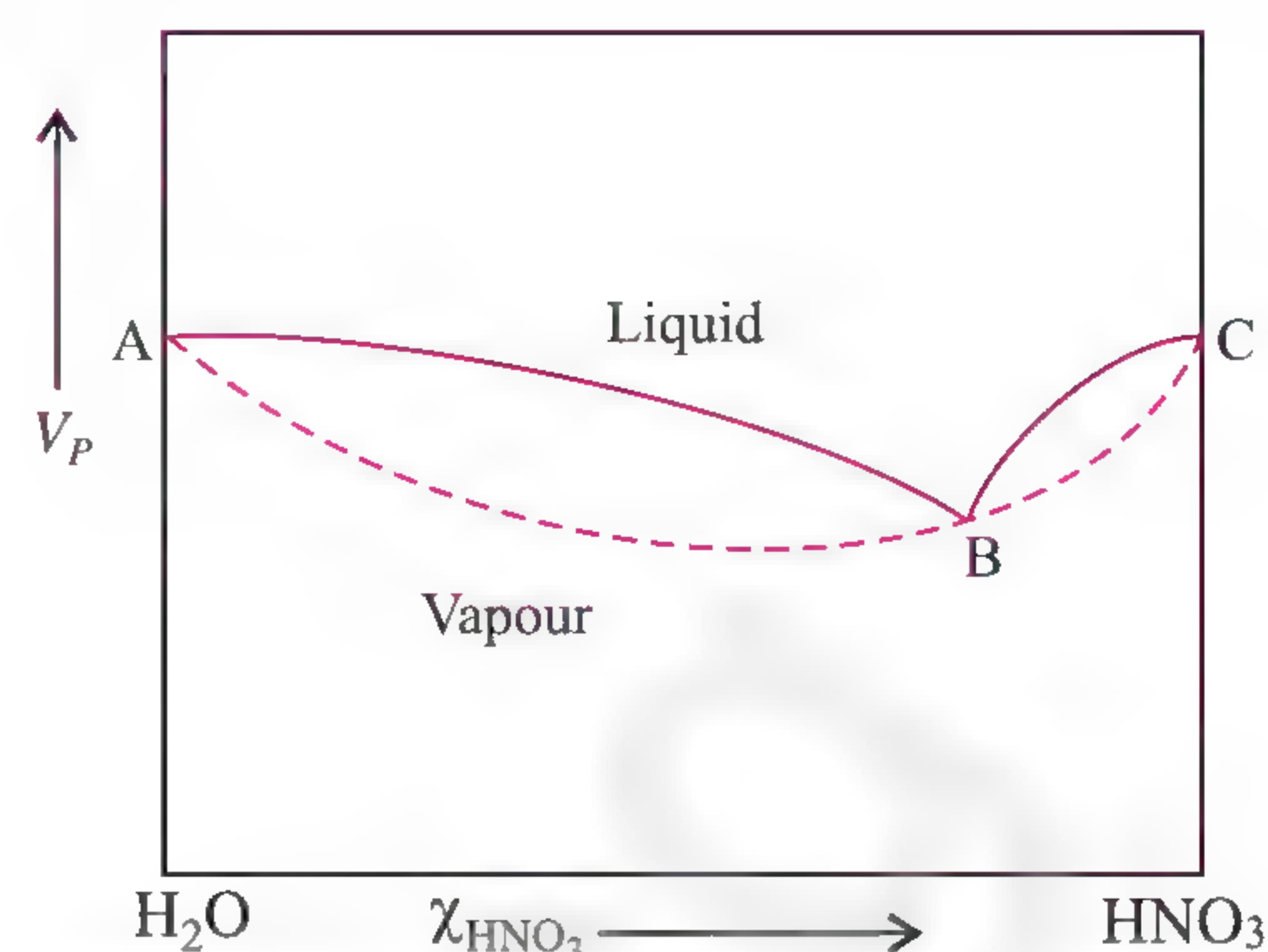


Fig. 2.14 Vapour pressure–composition diagram

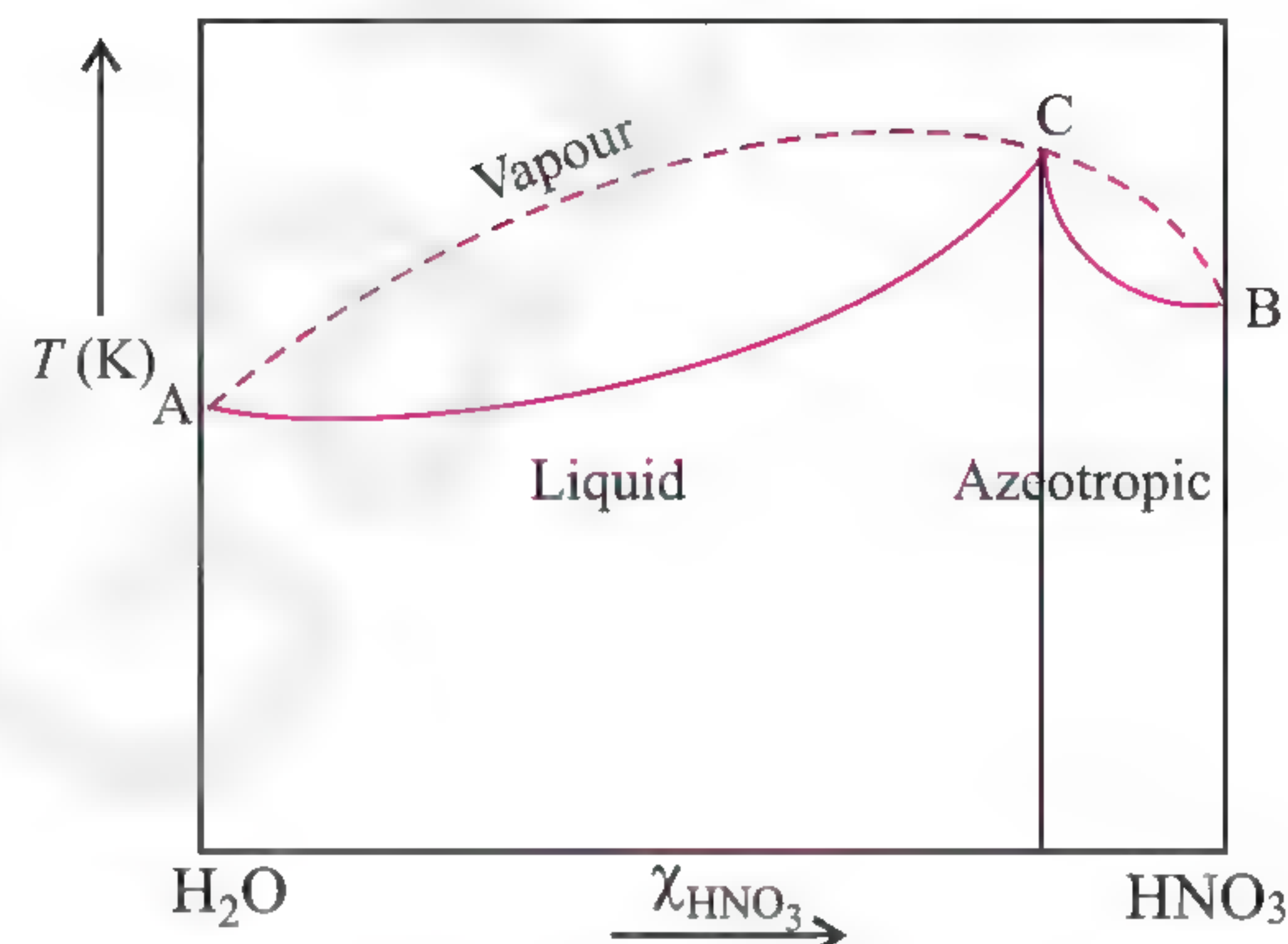


Fig. 2.15 Temperature–composition diagram

Table 2.4 Separation of azeotropes and preparation of absolute alcohol

Temperature	Azeotrope	Composition
331.8 K	Ternary azeotrope	H_2O : Benzene : Alcohol (7.4% : 74.1% : 18.5%)
341.2 K	Binary azeotrope	Benzene : Alcohol 67.7% : 32.2%
351 K	Absolute ethanol	

ILLUSTRATION 2.48

Why is an increase in temperature observed on mixing chloroform with acetone?

Sol. The bonds between chloroform molecules and molecules of acetone are dipole–dipole interactions, but on mixing, the chloroform and acetone molecules start forming hydrogen bonds which are stronger bonds resulting in the release of energy. This gives rise to an increase in temperature.

ILLUSTRATION 2.49

The dissolution of ammonium chloride in water is an endothermic process but still it dissolves in water readily. Why?

Sol. This is because of entropy change. In this case, ΔS is positive.



The ions that were held together in the crystalline solid are free and move in all possible directions. Its entropy increases and then $T \Delta S > \Delta H$.

ILLUSTRATION 2.50

Two liquids X and Y boil at 110°C and 130°C, respectively. Which one of them has higher vapour pressure at 50°C?

Sol. Lower the boiling point, more volatile it is. Hence, liquid X will have higher vapour pressure at 50°C.

ILLUSTRATION 2.51

Why does a solution of ethanol and cyclohexane show positive deviation from Raoult's law?

Sol. On adding cyclohexane, its molecules get in between the molecules of ethanol thus breaking the hydrogen bonds and reducing ethanol–ethanol interactions. This will increase the vapour pressure of the solution and result in positive deviation from Raoult's law.

ILLUSTRATION 2.52

What do you understand by colligative properties?

Sol. Colligative properties are those properties which depend upon the number of particles of solute but not on the nature of solute.

ILLUSTRATION 2.53

Name four important colligative properties of solutions of non-volatile solutes.

- Sol.**
- Relative lowering of vapour pressure
 - Elevation in boiling point
 - Depression in freezing point
 - Osmotic pressure

ILLUSTRATION 2.54

Cutting onions taken from the fridge is more comfortable than cutting those lying at room temperature. Explain why.

Sol. At lower temperature, the vapour pressure is low. Less vapours of the tear-producing chemicals are produced.

ILLUSTRATION 2.55

Define an ideal solution.

Sol. An ideal solution is a solution which follows Raoult's law, $\Delta_{\text{mix}}H = 0$, $\Delta_{\text{mix}}V = 0$. In ideal solution the force of attraction between A-B is equal to that in A-A and B-B.

ILLUSTRATION 2.56

Two liquids A and B on mixing produce a warm solution. Which type of deviation from Raoult's law does it show?

Sol. Warming up of the solution means that the process of mixing is exothermic, i.e., $\Delta_{\text{mixing}}H$ is negative. This implies that the solution shows a negative deviation.

ILLUSTRATION 2.57

What type of liquids form ideal solutions?

Sol. Liquids that have similar structures and polarities form ideal solutions.

ILLUSTRATION 2.58

Under what condition do non-ideal solutions show negative deviations?

Sol. When the new forces of interaction between the components are greater than those in the pure components, non-ideal solutions show negative deviations.

ILLUSTRATION 2.59

What are constant boiling mixtures called?

Sol. Azeotropes.

ILLUSTRATION 2.60

What are maximum boiling azeotropes? Give one example.

Sol. Maximum boiling azeotropes are those which boil at higher temperature than boiling point of each component in pure state, e.g., H_2O and HCl .

ILLUSTRATION 2.61

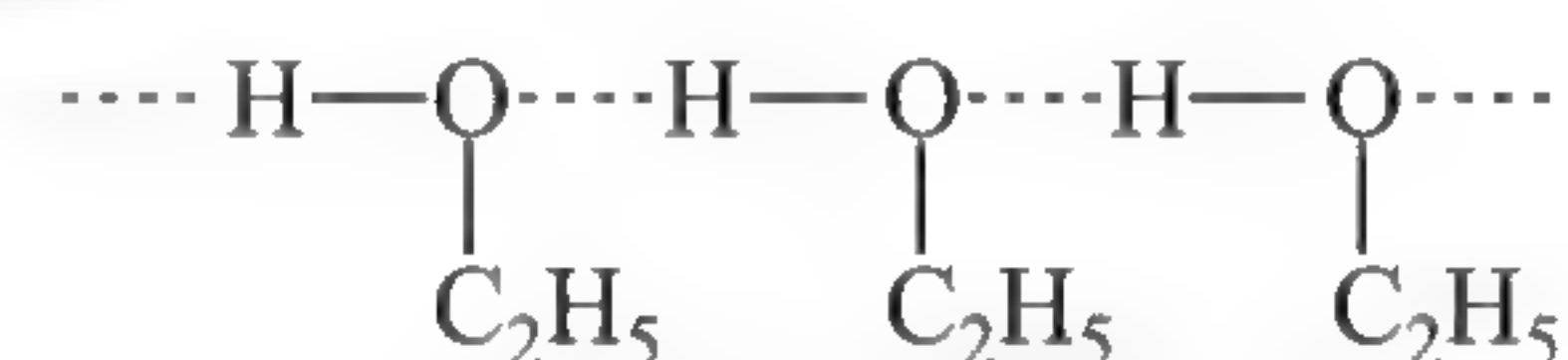
What are minimum boiling azeotropes? Give one example.

Sol. Minimum boiling azeotropes are those which boil at lower temperature than boiling point of each component in pure state, e.g., H_2O and $\text{C}_2\text{H}_5\text{OH}$.

ILLUSTRATION 2.62

Give one example each of miscible liquid pairs showing positive and negative deviation from Raoult's law. Give one reason for each for such deviations.

Sol. **Positive deviation from Raoult's law:** A mixture of ethanol and cyclohexane shows positive deviation. When pure ethanol is added to cyclohexane the molecules of cyclohexane come in between the molecules of ethanol which results in the breaking of hydrogen bonds and thus positive deviation.



Negative deviation from Raoult's law: A mixture of chloroform and acetone shows negative deviation. When these are mixed, hydrogen bond is formed and negative deviation is shown:

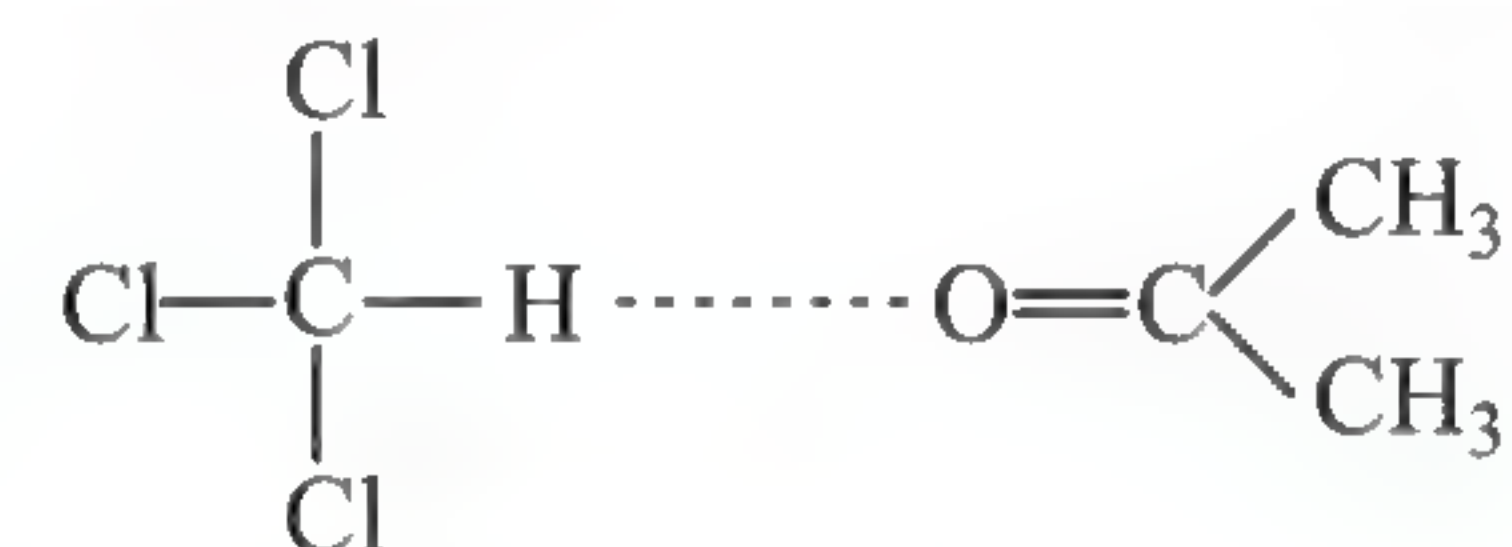


ILLUSTRATION 2.63

Can we separate the components of azeotropic mixture by distillation?

Sol. No, we cannot separate the components of an azeotropic mixture by distillation because at a particular composition, both the components boil at the same temperature.

2.10 COLLIGATIVE PROPERTIES

In this section we have learnt that the vapour pressure of a solution decreases when a non-volatile solute is added to a volatile solvent. There are many properties of solutions which are connected with this decrease of vapour pressure. These are: (a) relative lowering of the vapour pressure of the solvent, (b) depression in the freezing point of the solvent; (c) elevation in the boiling point of the solvent, and (d) osmotic pressure of the solution.

All the properties depend on the number of solute particles irrespective of their nature relative to the total number of particles present in the solution. Such properties are called *colligative properties* (colligative, from latin: *co* means together, *ligare* means to bind).

2.10.1 RELATIVE LOWERING OF VAPOUR PRESSURE

Recall that the vapour pressure of a solvent in a solution is less than that of pure solvent, that is because in solution only solvent molecules contribute to the total vapour pressure since the solute is non-volatile. Then, according to Raoult's law, the total vapour pressure of solution is equal to the mole fraction of solute multiplied to the vapour pressure of pure solvent, i.e.,

$$P_{\text{solution}} = \chi_{\text{solvent}} P_{\text{solvent}}^{\circ} \quad \dots(\text{i})$$

($P_{\text{solvent}}^{\circ}$ = vapour pressure of pure solvent, χ_{solvent} = mole fraction of solvent, P_{solution} = vapour pressure of solution)

The reduction in vapour pressure of solvent (ΔP_A) is given as

$$\Delta P_A = P_A^{\circ} - P_A \quad \dots(\text{ii})$$

$$= P_A^{\circ} - \chi_A P_A^{\circ} \quad \dots(\text{iii})$$

$$= P_A^{\circ} (1 - \chi_A) \quad \dots(\text{iv})$$

Knowing that $\chi_B = 1 - \chi_A$, i.e., total mole fraction is one.

Then, Eq. (iv) reduces to

$$\Delta P_A = P_A^{\circ} \chi_B \quad \dots(\text{v})$$

In a solution containing several non-volatile solutes, the lowering of the vapour pressure depends on the sum of the mole fraction of different solutes.

Equation (v) can be written as

$$\frac{\Delta P}{P_A^{\circ}} = \left(\frac{P_A^{\circ} - P_S}{P_A^{\circ}} \right) = \chi_B \quad \dots(\text{vi})$$

Equation (vi) is called the *relative lowering of vapour pressure* and is equal to the mole fraction of the solute.

Determination of Molar Mass of Solute from Relative Lowering of Vapour Pressure

The molecular mass of the solute can be determined by the relative lowering of vapour pressure. Equation (vi) can be rewritten as

$$\therefore \frac{P_A^{\circ} - P_S}{P_A^{\circ}} = \chi_B = \frac{n_B}{n_B + n_A} \quad \dots(\text{vii})$$

(where n_B and n_A are mole numbers of solute, and solvent, respectively)

$$n_B = \frac{W_B}{Mw_B}; n_A = \frac{W_A}{Mw_A}$$

(Mw_A ; Mw_B = molecular weight of solvent and solute, respectively; W_A , W_B = weight of solvent and solute, respectively)

$$\therefore \frac{P_A^{\circ} - P_S}{P_A^{\circ}} = \frac{\frac{W_B}{Mw_B}}{\frac{W_A}{Mw_A} + \frac{W_B}{Mw_B}} \quad \dots(\text{viii})$$

For a very dilute solution, $n_B \ll n_A$. Hence, n_B is negligible in comparison to n_A .

Then, Eq. (viii) reduces to

$$\frac{P_A^{\circ} - P_S}{P_A^{\circ}} = \frac{W_B}{Mw_B} \bigg/ \frac{W_A}{Mw_A} \quad \dots(\text{ix})$$

$$\text{or } \frac{P_{\text{solvent}}^{\circ} - P_{\text{solution}}}{P_{\text{solvent}}^{\circ}} = \frac{W_{\text{solute}} \times Mw_{\text{solvent}}}{Mw_{\text{solute}} \times W_{\text{solvent}}}$$

Thus, the molar mass of the solute can be determined if the other quantities, i.e., W_{solute} , W_{solvent} , Mw_{solvent} , and the relative lowering of vapour pressure $\left[\frac{P_{\text{solvent}}^{\circ} - P_{\text{solution}}}{P_{\text{solvent}}^{\circ}} \right]$, are known.

ALTERNATE FORMULA FOR THE RELATIVE LOWERING OF VAPOUR PRESSURE WHEN THE SOLUTION IS NOT DILUTE

$$\frac{P_{\text{solvent}}^{\circ} - P_{\text{solution}}}{P_{\text{solvent}}^{\circ}} \text{ or } \frac{P^{\circ} - P_S}{P^{\circ}} = \frac{n_B}{n_A + n_B} \quad \dots(\text{i})$$

On reversing Eq. (i), we get

$$\begin{aligned} \frac{P^{\circ}}{P^{\circ} - P_S} &= \frac{n_A + n_B}{n_B} = 1 + \frac{n_A}{n_B} \\ \Rightarrow \frac{P^{\circ}}{P^{\circ} - P_S} - 1 &= \frac{n_A}{n_B} \\ \Rightarrow \frac{P^{\circ} - P^{\circ} + P_S}{P^{\circ} - P_S} &= \frac{n_A}{n_B} \\ \Rightarrow \frac{P_S}{P^{\circ} - P_S} &= \frac{n_A}{n_B} \\ \text{or } \frac{P^{\circ} - P_S}{P_S} &= \frac{n_B}{n_A} \end{aligned}$$

Note: This equation can be used to solve the problem quickly, whether the solution is dilute or not.

Experimental Method for the Determination of Vapour Pressure Lowering

Static method

- Raoult's bassometric method
- Differential barrometric method

Dynamic method

- Ostwald and Walker method
- Differential barrometric method
- Transpiration method

Ostwald and Walker method: The relative lowering in vapour pressure is determined by Ostwald and Walker method. The experimental setup is shown in Fig. (2.16). It consists of two sets of bulbs. The first set of three bulbs is filled with solution. to half of their capacity and the second set of another three bulbs is filled with the pure solvent.

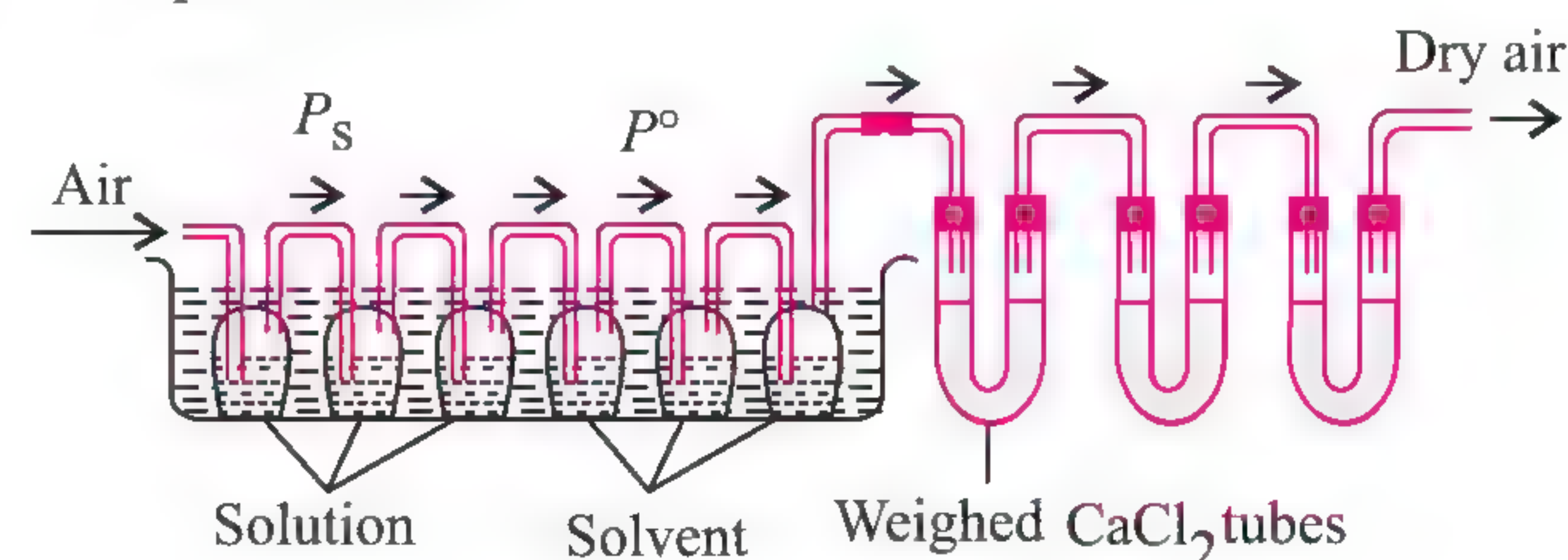


Fig. 2.16 Ostwald and Walker method

Each set is separately weighed accurately. Both sets are connected to each other and then with the accurately weighed set of guard tubes filled with anhydrous calcium chloride or some other dehydrating agents such as P_2O_5 , concentrated H_2SO_4 , etc.

The bulbs of solution and pure solvent are kept in a thermostat maintained at a constant temperature.

A current of pure dry air is bubbled through the series of bulbs as shown in Fig. 2.16. The air gets saturated with the vapours in each set of bulbs. The air takes up an amount of vapours proportional to the vapour pressure of the solution first and then it takes up more amount of vapour from the solvent which is proportional to the difference in the vapour pressure of solvent and the vapour pressure of solution, i.e., $P^\circ - P_S$. The two sets of bulbs are weighed again. The guard tubes are also weighed.

$$\text{Loss in mass in the solution bulbs} \propto P_S$$

$$\text{Loss in mass in the solvent bulbs} \propto (P^\circ - P_S)$$

$$\begin{aligned} \text{Total loss in the both sets of bulbs} &\propto [P_S + (P^\circ - P_S)] \\ &\propto P^\circ \end{aligned}$$

Total loss in the mass of both sets of bulbs is equal to gain in the mass of guard tubes.

$$\begin{aligned} \text{Thus, } \frac{P^\circ - P_S}{P^\circ} &= \frac{\text{Loss in mass in solvent bulbs}}{\text{Total loss in mass in both sets of bulbs}} \\ &= \frac{\text{Loss in mass in solvent bulbs}}{\text{Gain in mass of guard tubes}} \end{aligned}$$

Further we know from Raoult's law,

$$\frac{P^\circ - P_S}{P^\circ} = \frac{W_B/M_{w_B}}{W_A/M_{w_A} + W_B/M_{w_B}}$$

Hence,

$$\frac{\text{Loss in mass in solvent bulbs}}{\text{Gain in mass of guard tubes}} = \frac{W_B/M_{w_B}}{W_A/M_{w_A} + W_B/M_{w_B}}$$

The above relationship is used for the calculation of molecular masses of non-volatile solutes.

For very dilute solutions, the following relationship can be applied:

$$\frac{P^\circ - P_S}{P^\circ} = \frac{\text{Loss in mass in solvent bulbs}}{\text{Gain in mass of guard tubes}} = \frac{W_B/M_{w_B}}{W_A/M_{w_A}}$$

ILLUSTRATION 2.64

Calculate the molal lowering of vapour pressure for H_2O at 100°C .

$$\text{Sol. } \frac{P^\circ - P_S}{P^\circ} = \frac{n_2}{n_2 + n_1}$$

$$P^\circ - P_S = P^\circ \left[\frac{n_2}{n_2 + n_1} \right]$$

Let 1 mol of solute is dissolved in 1000 g solvent water.

$$\text{Thus, } n_2 = 1 \text{ and } n_1 = \frac{1000}{18}$$

Also, $P^\circ = 760 \text{ mm}$ for water at 100°C .

$$P^\circ - P_S = \left[\frac{1}{1 + \frac{1000}{18}} \right] \times 760 = 13.43 \text{ mm}$$

ILLUSTRATION 2.65

A current of dry air was bubbled through a bulb containing 26.66 g of an organic compound in 200 g of water, then through a bulb at the same temperature, containing water and finally through a tube containing anhydrous calcium chloride. The loss of mass in the bulb containing water was 0.087 g and the gain in the mass of the calcium chloride tube was 2.036 g. Calculate the molecular mass of the organic substance.

$$\begin{aligned} \text{Sol. } \frac{P^\circ - P_S}{P^\circ} &= \frac{\text{Loss in mass of solvent bulb}}{\text{Gain in mass of } \text{CaCl}_2 \text{ tube}} \\ &= \frac{0.087}{2.036} \end{aligned}$$

Let the molecular mass of the organic substance be M_{w_2} . According to Raoult's law,

$$\begin{aligned} \frac{P^\circ - P_S}{P^\circ} &= \frac{W_2/M_{w_2}}{\frac{W_2}{M_{w_2}} + \frac{W_1}{M_{w_1}}} \\ \frac{0.087}{2.036} &= \frac{\frac{26.66}{M_{w_2}}}{\frac{26.66}{M_{w_2}} + \frac{200}{18}} = \frac{26.66}{26.66 + \frac{200}{18} M_{w_2}} \end{aligned}$$

$$M_{w_2} = 53.75$$

ILLUSTRATION 2.66

What mass of non-volatile solute (urea) needs to be dissolved in 100 g of water in order to decrease the vapour pressure of water by 30%. What will be the molality of solution?

Sol. Using Raoult's law in the following form,

$$\frac{P^\circ - P_S}{P_S} = \frac{W_2 M_{w_1}}{W_1 M_{w_2}}$$

If $P^\circ = 100 \text{ mm}$, then $P_S = 70 \text{ mm}$

$$\frac{100 - 70}{70} = \frac{W_2 \times 18}{100 \times 60}$$

$$0.43 = \frac{W_2 \times 18}{100 \times 60} \Rightarrow W_2 = 143.33$$

$$\text{Molality} = \frac{W_2 \times 1000}{M_{w_2} \times W_1} = \frac{143.33 \times 1000}{60 \times 100} = 23.88$$

ILLUSTRATION 2.67

A solution containing 30 g of a non-volatile solute in exactly 90 g of water has a vapour pressure of 21.85 mm of Hg at 25°C . Further 18 g of water is then added to the solution; the new vapour pressure becomes 22.15 mm of Hg at 25°C . Calculate the (a) molecular mass of the solute and (b) vapour pressure of water at 25°C .

Sol. Let the vapour pressure of water at 25°C be P° and molecular mass of the solute be M_{w_2} .

Using Raoult's law in the following form,

$$\frac{P^\circ - P_S}{P_S} = \frac{W_2 M_{w_1}}{W_1 M_{w_2}}$$

$$\text{For solution (I), } \frac{(P^\circ - 21.85)}{21.85} = \frac{M}{2} \quad \dots(i)$$

$$\text{For solution (II), } \frac{(P^\circ - 22.15)}{22.15} = \frac{30 \times 18}{108 \times M_{w_2}} \quad \dots(ii)$$

Dividing Eq. (i) by Eq. (ii), we get

$$\frac{(P^\circ - 21.85)}{21.85} \times \frac{22.15}{(P^\circ - 22.15)} = \frac{108}{90} = \frac{6}{5}$$

$$P^\circ = 23.87 \text{ mm of Hg}$$

Substituting the value of P° in Eq. (i), we get

$$M_{w_2} = 67.9$$

ILLUSTRATION 2.68

The vapour pressure of a dilute aqueous solution of glucose is 700 mm Hg at 370 K. Calculate the (a) molality and (b) mole fraction of the solute.

Sol. P° = Vapour pressure of water at 373 K = 760 mm Hg

Using Raoult's law in the following form,

$$\frac{P^\circ - P_s}{P_s} = \frac{W_2 M_{w_1}}{W_1 M_{w_2}}$$

$$\text{or } \frac{760 - 700}{700} = \frac{W_2 \times 18}{W_1 \times M_{w_2}}$$

$$\text{or } \frac{W_2}{W_1 \times M_{w_2}} = \frac{60}{700 \times 18}$$

$$\text{Molality} = \frac{W_2}{W_1 \times M_{w_2}} \times 1000 = \frac{60 \times 1000}{700 \times 18} = 4.76 \text{ m}$$

$$P_s = \text{Mole fraction of solvent} \times P^\circ;$$

$$\text{Mole fraction of solvent} = \frac{700}{760} = 0.921$$

$$\text{So, mole fraction of solute} = 1 - 0.921 = 0.0789$$

ILLUSTRATION 2.69

10 g of glucose (molar mass 180) and 20 g of sucrose (molar mass 342) are dissolved in 100 g of water. What will be the vapour pressure of the resultant solution if the vapour pressure of water is 30 mm Hg?

Sol. Mass of glucose = 10 g

$$\text{Number of moles of glucose} = 0.0556$$

$$\text{Mass of sucrose} = 20 \text{ g}$$

$$\text{Number of moles of sucrose} = 0.0585$$

$$\text{Mass of water} = 100 \text{ g}$$

$$\text{Number of moles of water} = 5.556$$

$$\text{Total number of moles} = 5.556 + 0.0585 + 0.0556 = 5.67$$

$$\text{Mole fraction of water} = \frac{5.556}{5.67}$$

$$\text{Vapour pressure of solution} = \text{Mole fraction of water} \times P^\circ$$

$$= \frac{5.556}{5.67} \times 30 = 29.3 \text{ mm Hg}$$

ILLUSTRATION 2.70

Calculate the vapour pressure of an aqueous solution of 1.0 molal glucose solution at 100°C.

$$\text{Sol. } \text{Molality} = \frac{W_2}{M_{w_2} \times W_1} \times 1000$$

where W_2 = mass of solute in grams;

W_1 = mass of solvent in grams

$$1.0 = \frac{W_2 \times 1000}{M_{w_2} \times W_1}$$

$$\text{or } \left(\frac{K}{W_1} = K' \right) = \frac{1.0}{1000} = 0.001$$

Applying Raoult's law for dilute solution,

$$\frac{P^\circ - P_s}{P^\circ} = \frac{W_2}{M_{w_2} \times W_1} \times M_{w_1} \quad [M_{w_1} = 18]$$

$$\frac{760 - P_s}{760} = 0.001 \times 18 \quad [P^\circ = 760 \text{ mm at } 100^\circ\text{C}]$$

$$\begin{aligned} \text{or } P_s &= 760 - 760 \times 0.001 \times 18 \\ &= 760 - 13.68 \\ &= 746.32 \text{ mm Hg} \end{aligned}$$

ILLUSTRATION 2.71

The vapour pressure of pure benzene at 50°C is 268 mm of Hg. How many moles of non-volatile solute per mole of benzene are required to prepare a solution of benzene having a vapour pressure of 160.0 mm of Hg at 50°C?

Sol. Applying Raoult's law in the following form:

$$\frac{P^\circ - P_s}{P_s} = \frac{W_2 / M_{w_2}}{W_1 / M_{w_1}}$$

= Number of moles of solute per mole of benzene

$$\text{or } \frac{n_2}{n_1} = \frac{(268 - 160)}{160} = 0.675$$

Alternative method

We know that $P_s = \text{Mole fraction of solvent} \times P^\circ$

$$\text{or } 160 = \text{Mole fraction of solvent} \times 268$$

$$\text{So, molar fraction of solvent} = \frac{160}{268} = 0.597$$

$$\text{Mole fraction of solute} = 1 - 0.597 = 0.403$$

$$\frac{n_2}{n_1} = \frac{\text{Mole fraction of solute}}{\text{Mole fraction of solvent}} = \frac{0.403}{0.597} = 0.675$$

ILLUSTRATION 2.72

Lowering of vapour pressure due to a solute in 1 molal aqueous solution at 100°C is

- | | |
|----------------|----------------|
| a. 13.44 mm Hg | b. 14.12 mm Hg |
| c. 13.2 mm Hg | d. 35.2 mm Hg |

Sol. a. $M_{w_B} = \frac{\chi_B \times 1000}{(1 - \chi_B)M_{w_A}}$

$$1 = \frac{\chi_B \times 1000}{(1 - \chi_B) \times 18} \quad \left[\begin{array}{l} \chi_B = \text{mole fraction of solute} \\ M_{w_A} = \text{molar mass of solvent} \end{array} \right]$$

$$\chi_B = 0.0176$$

$$\chi_A = 1 - 0.0176 = 0.9824$$

$$P = P^\circ \chi_A = 760 \times 0.9824 = 746.62$$

$$\Delta P = P^\circ - P = 760 - 746.62 \approx 13.41$$

ILLUSTRATION 2.73

Calculate the vapour pressure lowering caused by the addition of 68.4 g of sucrose (molecular mass = 342) to 500 g of water if the vapour pressure of pure water at 25°C is 20.0 mm Hg.

Sol. According to Raoult's law.

$$\frac{P^\circ - P_s}{P^\circ} = \frac{n_2}{n_2 + n_1} = \chi_2$$

$$\text{or } \Delta P = \frac{n_2}{n_2 + n_1} P^\circ$$

$$\text{Given: } n_2 = \frac{68.4}{342} = 0.20 : n_1 = \frac{500}{18} = 27.78 \text{ and } P^\circ = 20.0$$

Substituting the values in the above equation, we get

$$\Delta P = \frac{0.20}{0.20 + 27.78} \times 20.0 = 0.142 \text{ mm Hg}$$

ILLUSTRATION 2.74

Calculate the vapour pressure of an aqueous solution which contains 5 mass per per cent of urea. The vapour pressure of pure water is 23.5 mm Hg. The molar mass of urea is 60.

Sol. Mass of urea = 5 g

$$\text{Mass of water} = (100 - 5) = 95 \text{ g}$$

$$\text{Number of moles of urea} = \frac{5}{60} = 0.083$$

$$\text{Number of moles of water} = \frac{95}{18} = 5.278$$

$$\begin{aligned} \text{Total number of moles} &= 5.278 + 0.083 \\ &= 5.301 \end{aligned}$$

$$\text{Mole fraction of solvent} = \frac{5.278}{5.361}$$

$$\begin{aligned} P_s &= \text{Mole fraction of solvent} \times P^\circ \\ &= \frac{5.278}{5.361} \times 23.5 = 23.14 \text{ mm Hg} \end{aligned}$$

ILLUSTRATION 2.75

The relative lowering of the vapour pressure of an aqueous solution containing a non-volatile solute is 0.0125. The molality of the solution is

- | | |
|---------|---------|
| a. 0.80 | b. 0.50 |
| c. 0.70 | d. 0.40 |

Sol. c. As we know

$$\frac{P^\circ - P}{P^\circ} = \chi_2 = \text{mole fraction of solute}$$

The ratio $(P^\circ - P)/P^\circ$ is the relative lowering of vapour pressure, which is equal to 0.0125 here.

$$\therefore \chi_2 = 0.0125$$

The relation between m and χ is:

$$\begin{aligned} m &= \frac{\chi_2 \times 1000}{\chi_1 \times M_{w_1}} = \frac{0.0125 \times 1000}{(1 - 0.0125) \times 18} \left[\begin{array}{l} M_{w(\text{H}_2\text{O})} \\ = 18 \text{ g mol}^{-1} \end{array} \right] \\ &= \frac{0.0125 \times 1000}{0.9875 \times 18} = 0.70 \end{aligned}$$

$$\therefore m = 0.70$$

ILLUSTRATION 2.76

A current of air was bubbled through a bulb containing 7.5 g of an organic substance in 75 g of H_2O , then through pure water and finally through a U-tube containing fused CaCl_2 . The loss in the weight of the first tube was 2.81 g and the gain in the weight of U-tube was 2.864 g. Calculate the molecular weight of organic substance.

Sol. (Ostwald and Walker's method)

a. Loss in weight of first bulb containing solvent (let W_1) is $W_1 \propto P_s$

b. Loss in weight of second bubble containing solvent (let W_2) is $W_2 \propto P^\circ - P_s$.

c. Gain in weight of CaCl_2 tube ($W_1 + W_2$) is $W_1 + W_2 \propto P_s + P^\circ - P_s$

$$\therefore W_1 + W_2 \propto P^\circ$$

$$P^\circ - P_s = 2.864 - 2.81 = 0.054$$

$$\therefore \frac{P^\circ - P_s}{P^\circ} = \frac{W_2}{W_1 + W_2}$$

$$\frac{0.054}{2.864} = \frac{7.5}{\frac{M_{w_2}}{18}} \Rightarrow M_{w_2} = 95.46$$

ILLUSTRATION 2.77

At 25°C, the vapour pressure of pure water is 25.0 mm Hg and that of an aqueous dilute solution of urea is 20 mm Hg. Calculate the molality of the solution.

Sol. The given values are:

$$P_A^\circ = 25 \text{ mm Hg}, P_s = 22 \text{ mm Hg}$$

$$m = ?$$

Using Raoult's law

$$\frac{P_A^\circ - P_s}{P_A^\circ} = \chi_B$$

Substituting all the values

$$\chi_B = \frac{25 - 20}{25} = 0.20$$

$$\therefore \chi_A = 1 - \chi_B = 1 - 0.2 = 0.8$$

The relationship between molality and mole fraction of solute in a dilute solution is

$$m = \frac{\chi_B}{\chi_A M_{w_A}} \times 1000, \text{ where } M_{w_A} = \text{molar mass of solvent}$$

$$= \frac{0.2 \times 1000}{0.8 \times 18} = 13.8$$

Molality of solution is 13.8.

ILLUSTRATION 2.78

Equal amounts of a solute are dissolved in equal amounts of two solvents A and B. The lowering of vapour pressure for solution A has twice the lowering of vapour pressure for solution B. If M_{w_A} and M_{w_B} are the molecular weights of solvents A and B, respectively, then

- a. $M_{w_A} = M_{w_B}$ b. $M_{w_A} = M_{w_B}/2$
 c. $M_{w_A} = 4M_{w_B}$ d. $M_{w_A} = 2M_{w_B}$

Sol. d. Let solute (i) is added to solvents A and B.

For A

$$\frac{P_i^\circ - P_s}{P_i^\circ} = \chi_i \approx \frac{M_{w_A}}{M_{w_i}}$$

For B

$$\frac{P_i^\circ - P_s}{P_i^\circ} = \chi_i \approx \frac{M_{w_B}}{M_{w_i}}$$

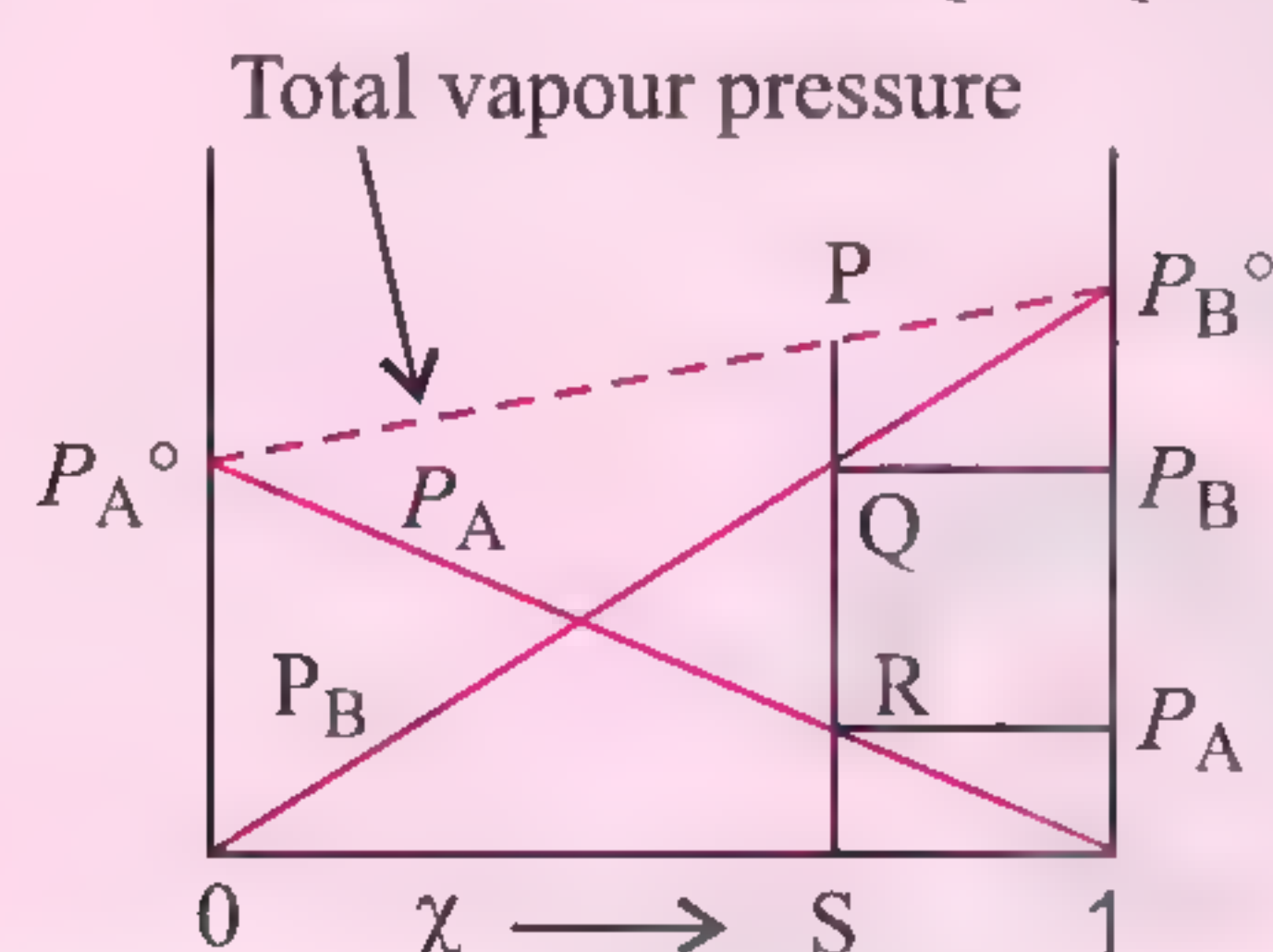
Given that lowering for solution A is twice to B

$$\therefore \frac{M_{w_A}}{M_{w_i}} = 2 \left(\frac{M_{w_B}}{M_{w_i}} \right) \Rightarrow M_{w_A} = 2M_{w_B}$$

ILLUSTRATION 2.79

Consider the following vapour pressure– composition graph. SP is equal to:

- a. PQ + RS b. PQ + QR
 c. SR + SQ d. PQ + QR + RS



Sol. c. According to Dalton's rule: Total pressure of a gaseous solution is equal to the sum of partial pressure,

$$\therefore P_{\text{total}} = P_A + P_B$$

$$= SR + SQ$$

2.10.2 ELEVATION IN BOILING POINT

A liquid starts boiling when its vapour pressure becomes equal to the external pressure. The temperature at which this occurs is known as the boiling point of the liquid. If the external pressure is 1 atm, this temperature is known as the normal boiling point of the liquid. When a non-volatile solute is added to a liquid solvent the vapour pressure of the solution becomes comparatively smaller than that of the pure solvent (Raoult's law). Consequently the temperature at which the vapour pressure of solution becomes

equal to the external pressure, will be greater than that of pure solvent, thus raising its boiling point. As we know that the decrease in vapour pressure is directly proportional to the mole fraction of the solute in the solution, it is therefore expected that the corresponding increase in the boiling point also depends on the amount fraction of the solute in the solution.

The elevation in boiling point on the addition of a non-volatile solute to a solvent can be easily illustrated graphically in Fig. 2.17.

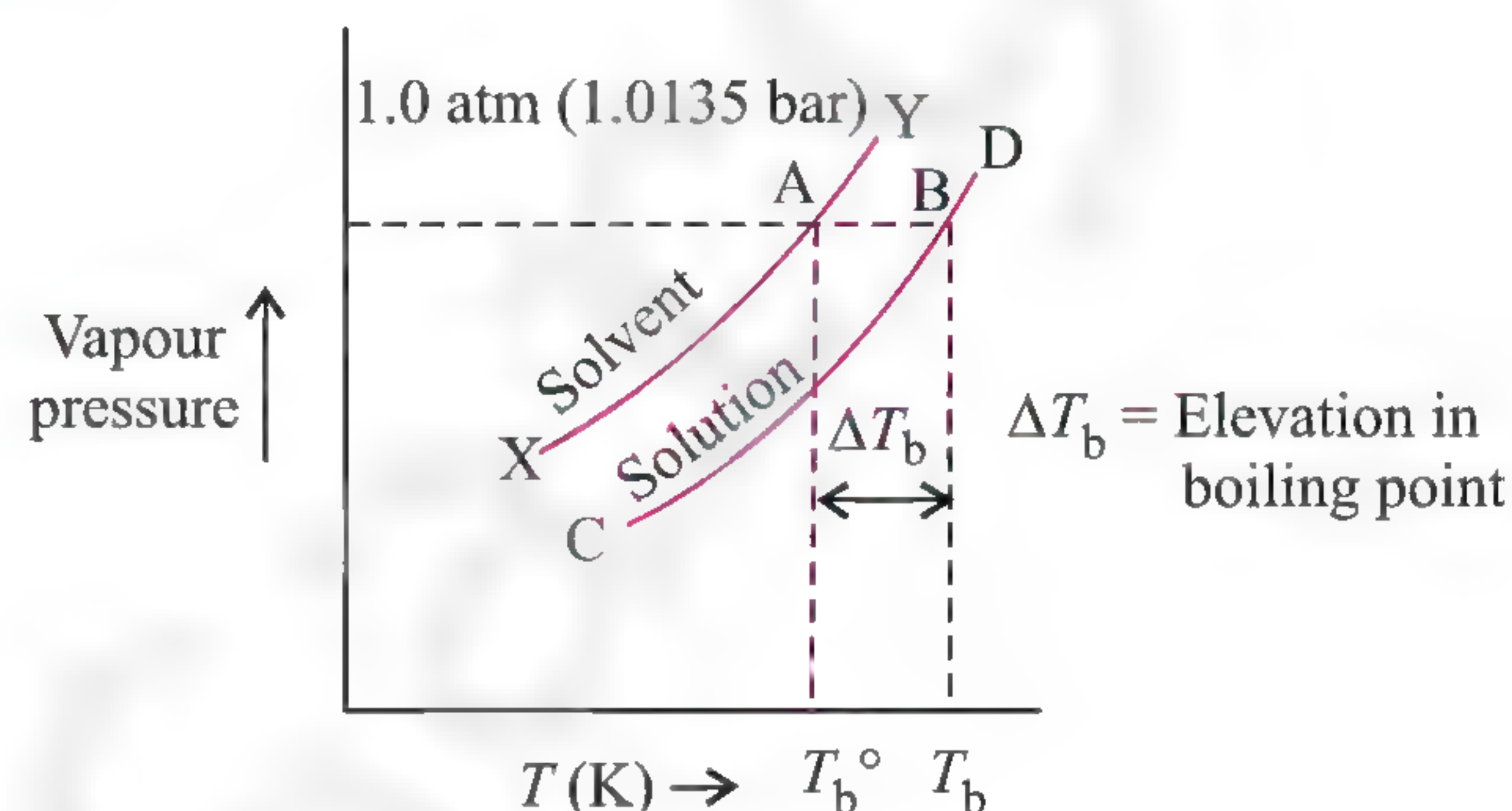


Fig. 2.17 Elevation in boiling point

Figure 2.17 shows the variation of vapour pressure with rise in temperature for solvent and solution. The curve XY gives the variation in vapour pressure for pure solvent and the curve CD gives the variation of vapour pressure for solution at different temperature. The curve CD lies below to XY because the vapour pressure of the solution is less than that of the pure solvent at all temperatures.

It is clear from the figure that at atmospheric pressure 1 atm the curve of vapour pressure for solvent XY and for solution CD intersect at A and B. A and B on temperature axis correspond to boiling point of pure solvent (T_b°) and boiling point of solution (T_b), respectively.

Thus, the boiling point of pure solvent T_b° is lower than that of solution (T_b). Hence there is an elevation or increase in the boiling temperature of the solution as compared to that of the solvent.

The boiling point elevation depends on the amount of solute and experimentally it has been shown that the elevation in boiling point is directly proportional to the molal concentration of the solute in the solution.

$$\text{i.e., } \Delta T_b \propto m \text{ or } \Delta T_b = K_b m \quad \dots(i)$$

Here m (molality) is the number of moles of solute in 1 kg of solvent and the constant K_b is called *boiling point elevation constant* (or ebullioscopic constant). The unit of K_b is K kg mol^{-1} .

DERIVATION FOR THE ELEVATION IN BOILING POINT

The elevation in boiling point (ΔT_b),

$$\Delta T_b = \text{Boiling point of solution} - \text{Boiling point of pure solvent}$$

This can be better understood by plotting a graph of vapour pressure against temperature for a pure solvent and two solutions of different concentrations. The curve of the solutions is always below the curve of the pure solvent. T_0 , T_1 , and T_2 represent the boiling points of pure solvent, solution I, and solution II,

respectively. The vapour pressure of pure solvent, solution I, and solution II at temperature T_0 are P° , P_1 , and P_2 , respectively.

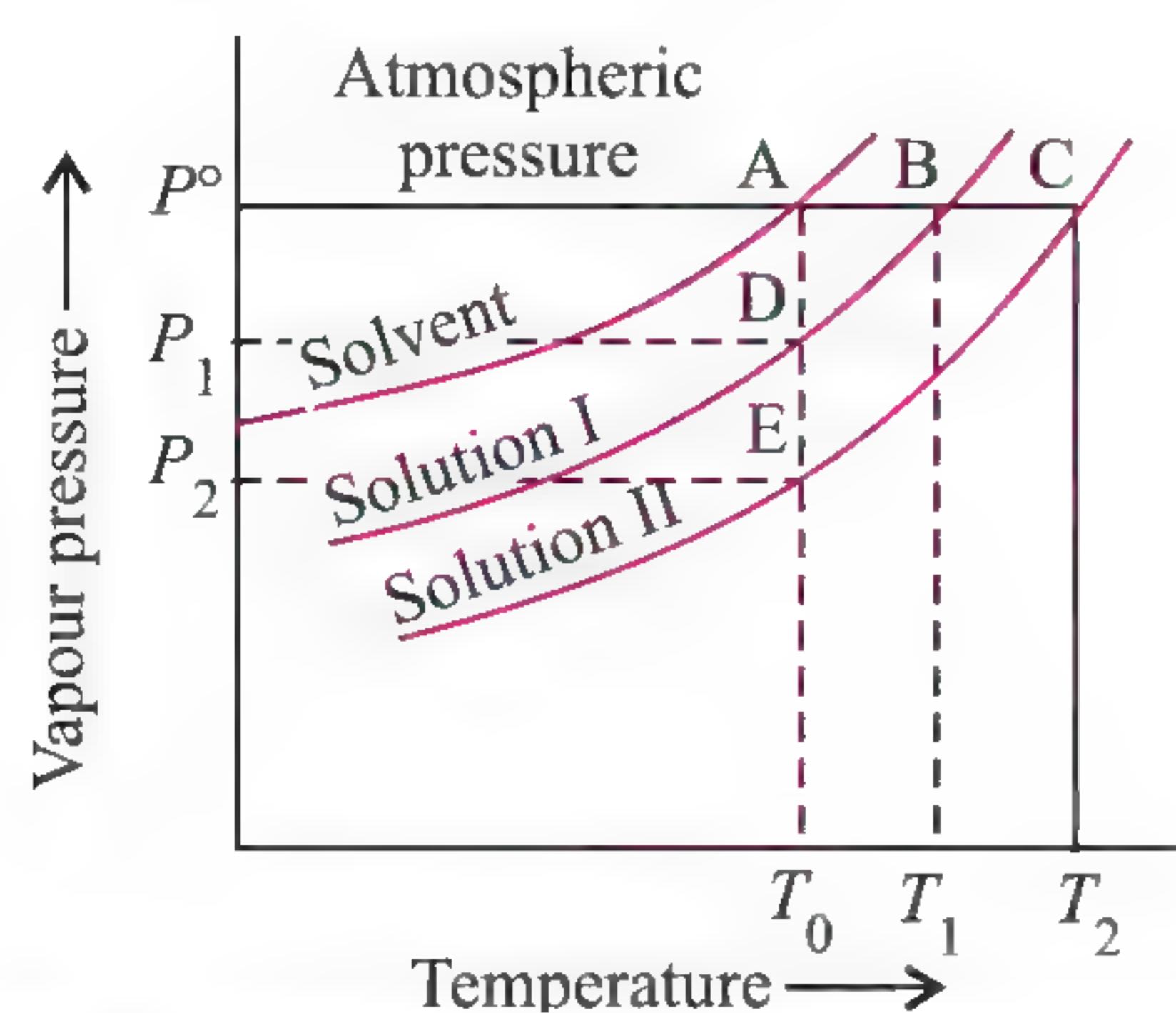


Fig. 2.18 Vapour-pressure-temperature curves

Assuming that the solutions are very dilute, these curves may be approximately taken as straight lines near the boiling point. Thus, $\triangle ACE$ and $\triangle ABD$ are similar.

$$\therefore \frac{AC}{AB} = \frac{AE}{AD}$$

$$\text{or } \frac{T_2 - T_0}{T_1 - T_0} = \frac{P^\circ - P_2}{P^\circ - P_1}$$

$$\text{or } \frac{\Delta T_2}{\Delta T_1} = \frac{\Delta P_2}{\Delta P_1}$$

$$\text{or } \Delta T \propto \Delta P$$

From Raoult's law for dilute solution,

$$\frac{P^\circ - P_s}{P^\circ} = \frac{W_B \times M_{w_A}}{M_{w_B} \times W_A}$$

(P_s = vapour pressure of solution)

$$\text{or } P^\circ - P_s = \frac{W_B \times M_{w_A}}{M_{w_B} \times W_A} P^\circ$$

For the pure solvent, P° (its vapour pressure at the boiling point) and M_{w_A} (its molecular mass) are constant.

$$\therefore P^\circ - P_s \propto \frac{W_B}{M_{w_B} W_A}$$

$$\text{or } \Delta P \propto \Delta T \propto \frac{W_B}{M_{w_B} W_A}$$

$$\text{or } \Delta T = K \cdot \frac{W_B}{M_{w_B} W_A} \quad \dots(i)$$

where K is a constant, called as elevation constant.

When $\frac{W_B}{M_{w_B}} = 1$, (one mole of solute) and $W_A = 1000$ g, then

$$\Delta T = \frac{K}{1000} = K_b$$

where K_b is called molal elevation constant. It is defined as the elevation in boiling point produced when 1 mole of the solute is dissolved in 1000 g of the solvent.

Thus, $K = 1000K_b$

Putting this values in Eq. (i)

$$\Delta T^* = \frac{1000K_b W_B}{M_{w_B} W_A} \quad \dots(ii)$$

$$\text{or } \Delta T = \text{Molality} \times K_b$$

$$\left(\text{Since } \frac{W_B}{M_{w_B} \times W_A} \times 1000 = \text{Molality} \right)$$

The elevation the boiling point of a solution of non-electrolyte is proportional to its molality and equimolal solutions of all the substances in the same solvent will show equal elevation in boiling points. These are known as Raoult's laws of elevation in boiling point.

MOLAL ELEVATION CONSTANT AND ENTHALPY OF VAPOURIZATION

The molal elevation constant is characteristic of a particular solvent and can be calculated from the thermodynamical relationship.

$$K_b = \frac{M_{w_A} R T_b^2}{\Delta_{\text{vap}} H \times 1000} \quad \text{or} \quad K_b = \frac{R T_b^2}{l_v \times 1000}$$

where M_{w_A} is the molar mass of solvent, T is the boiling point of solvent, R is the gas constant, and $\Delta_{\text{vap}} H$ is the molar enthalpy of vapourization of the solvent. l_v is the latent heat of vapourization.

Following are the experimental methods for the determination of the elevation in boiling point (ΔT_b):

- Beckmann's method
- Cottrell's method

ILLUSTRATION 2.80

2 g each of two solutes A and B (molar mass of A is greater than that of B) are dissolved separately in 50 g each of the same solvent. Which will show greater elevation in the boiling point?

Sol. The solution containing solute B will show greater elevation in the boiling point because $\Delta T_b \propto \frac{1}{M_w}$.

ILLUSTRATION 2.81

Distinguish between the boiling point of a liquid and the normal boiling point of a liquid.

Sol. The boiling point is the temperature at which the vapour pressure of the liquid becomes equal to the surrounding pressure. The normal boiling point is the temperature at which the vapour pressure is 1 atm.

ILLUSTRATION 2.82

Explain why the melting point of a substance gives an indication of the purity of a substance.

Sol. Impurities cause depression in freezing point (melting point). More the impurities, lower is the freezing point.

ILLUSTRATION 2.83

What happens to the vapour pressure of water if a table spoon of sugar is added to it?

Sol. Addition of non-volatile solute lowers the vapour pressure of solvent (water).

ILLUSTRATION 2.84

Define molal elevation constant or ebullioscopic constant.

Sol. Molal elevation constant is defined as the elevation in boiling point that takes place when the molality of solutions is unity.

ILLUSTRATION 2.85

Two liquids A and B boil at 130°C and 160°C, respectively. Which of the them has higher vapour pressure at 80°C.

Sol. Liquid A with lower boiling point is more volatile and therefore will have higher vapour pressure.

ILLUSTRATION 2.86

Match the following if the molar mass of X, Y, and Z are same:

Solvent	$T_b(^{\circ}\text{C})$	$K_b (\text{kg K mol}^{-1})$
X	127	0.73
Y	27	0.53
Z	253	0.98

Sol. Since $K_b = \frac{RT_b^2}{1000\Delta_{\text{vap}}H/M_{w_{\text{solvent}}}}$, we have

$$K_b = \frac{RT_b}{1000\left(\frac{\Delta_{\text{vap}}H}{T_b}\right)/M_{w_{\text{solvent}}}} = (\text{constant}) T_b$$

$$\left[\frac{\Delta_{\text{vap}}H}{T_b} \text{ is taken to be constant as per Trouton's rule}\right]$$

$$\Rightarrow K_b \propto T_b$$

Thus, we have

$$K_b (\text{X}) = 0.73 \text{ kg K mol}^{-1}; K_b (\text{Y}) = 0.531 \text{ kg K mol}^{-1};$$

$$K_b (\text{Z}) = 0.98 \text{ kg K mol}^{-1}$$

ILLUSTRATION 2.87

The boiling point of a solution made by dissolving 12.0 g of glucose in 100 g of water is 100.34°C. Calculate the molecular weight of glucose; K_b for water = 0.52°C/m.

Sol. Using the relation for the molecular weight of a solute from elevation in boiling point, we have

$$\begin{aligned} M_{w_B} &= K_b \left(\frac{W_B}{W_A \Delta T_b} \times 1000 \right) \\ &= 0.52 \left(\frac{12}{100 \times 0.34} \times 1000 \right) \\ &\quad (\Delta T_b = 100.34 - 100 = 0.34^{\circ}\text{C}) \\ \Rightarrow M_{w_B} &= 183.5 \text{ g mol}^{-1} \end{aligned}$$

ILLUSTRATION 2.88

A solution containing 0.2563 g of naphthalene (molecular mass = 128) in 50 g of carbon tetrachloride yields a boiling point elevation of 0.201°C while a solution of 0.6216 g of an unknown solute in the same mass of the solvent gives a boiling point elevation of 0.647°C. Find the molecular mass of unknown solute.

Sol. We know that

$$K_b = \frac{\Delta T_b \times W_1 \times M_{w_2}}{1000 \times W_2}$$

$$\text{For } \text{CCl}_4; K_b = \frac{0.201 \times 50 \times 128}{1000 \times 0.2563} = 5.019$$

$$\begin{aligned} M_{w_2} &= \frac{1000 \times K_b \times W_2}{\Delta T_b \times W_1} \\ &= \frac{1000 \times 5.019 \times 0.6216}{0.647 \times 50} = 96.44 \end{aligned}$$

ILLUSTRATION 2.89

The boiling point elevation constant for benzene is 2.57°C/m. The boiling point of benzene is 81.0°C. Determine the boiling point of a solution formed when 5 g of $\text{C}_{14}\text{H}_{12}$ is dissolved in 15 g of benzene.

Sol. Given weight of $\text{C}_{14}\text{H}_{12}$ (W_B) = 5 g

Weight of benzene (W_A) = 15 g

$$\begin{aligned} \Delta T_b &= K_b \left[\frac{W_B \times 1000}{M_{w_B} W_A} \right] \\ &= 2.57 \left[\frac{5 \times 1000}{180 \times 15} \right] = 4.76^{\circ}\text{C} \end{aligned}$$

$$\text{Now, } \Delta T_b = T_b - T_b^{\circ} \quad \begin{cases} T_b^{\circ} = \text{boiling point of pure solvent} \\ T_b = \text{boiling point of solution} \end{cases}$$

$$\begin{aligned} \therefore T_b &= \Delta T_b + T_b^{\circ} \\ &= 4.76 + 81.0 \\ &= 85.76^{\circ}\text{C} \end{aligned}$$

ILLUSTRATION 2.90

12.2 g of benzoic acid is dissolved in (i) 1 kg acetone ($K_b = 1.9 \text{ K kg mol}^{-1}$) and (ii) 1 kg benzene ($K_b = 2.6 \text{ K kg mol}^{-1}$). The elevations of boiling points are 0.19°C and 0.13°C, respectively.

- What are the molar masses of benzoic acid in the two solutions?
- What are the structures of benzoic acid in the two solutions?

Sol. Let M_{w_B} be the molar mass of benzoic acid in the two solutions.

The molality of the solution is:

$$m = \frac{n_B}{W_A} = \frac{(12.2 \text{ g}) / M_{w_B}}{1 \text{ kg}}$$

Since $\Delta T_b = K_b m$, we get:

a. i. Acetone solution

$$0.19 \text{ K} = (1.9 \text{ K kg mol}^{-1}) \left[\frac{12.2 \text{ g}/M_{w_{\text{benzoic acid}}}}{1 \text{ kg}} \right]$$

$$M_{w_{\text{benzoic acid}}} = \frac{1.9 \times 12.2}{0.19} \text{ g mol}^{-1} = 122 \text{ g mol}^{-1}$$

ii. Benzene solution

$$0.13 \text{ K} = (2.6 \text{ K kg mol}^{-1}) \left[\frac{12.2 \text{ g}/M_{w_{\text{benzoic acid}}}}{1 \text{ kg}} \right]$$

$$M_{w_{\text{benzoic acid}}} = \frac{2.6 \times 12.2}{0.13} \text{ g mol}^{-1} = 244 \text{ g mol}^{-1}$$

b. The actual molar mass of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) is 122 g mol^{-1} . This means benzoic acid is present as a monomer in acetone solution while it dimerizes in benzene solution. The structure of dimerized benzoic acid is

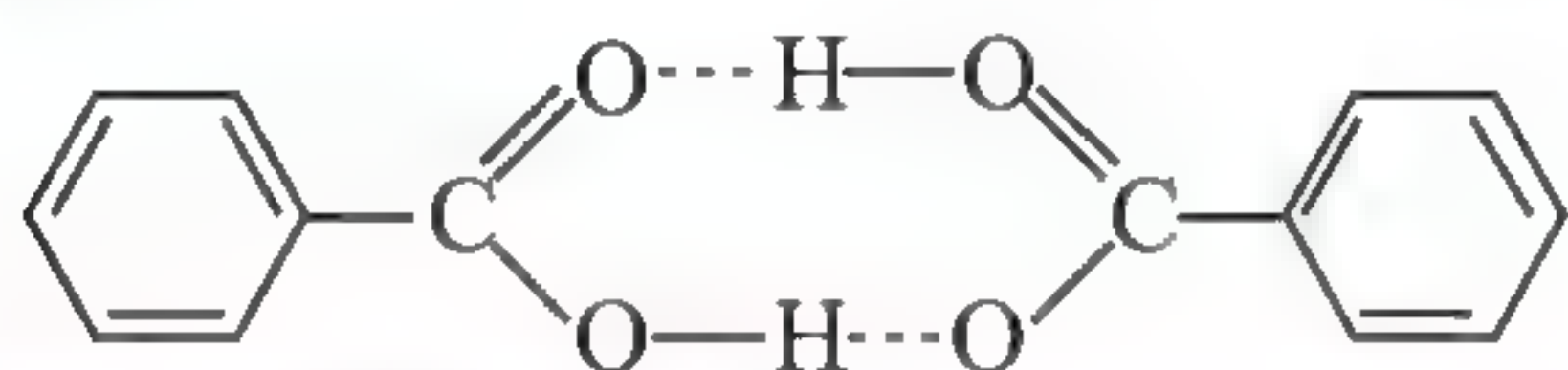


ILLUSTRATION 2.91

The ebullioscopic constant for benzene is 2.52 K m^{-1} . A solution of an organic substance in benzene boils at 0.125°C higher than benzene. Calculate the molality of solution?

Sol. Given values are:

$$K_b = 2.52 \text{ K m}^{-1} \text{ or } 2.52 \text{ K kg mol}^{-1}$$

$$\Delta T_b = 0.125^\circ\text{C}$$

Using the relation, $\Delta T_b = K_b m$

$$\begin{aligned} \therefore m &= \frac{\Delta T_b}{K_b} \\ &= \frac{0.125}{2.52} = 0.05 \end{aligned}$$

Hence, molality of the solution is 0.05 m .

ILLUSTRATION 2.92

18 g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is dissolved in 1 kg of water in a saucepan. At what temperature will the water boil (at 1 atm)? K_b for water is $0.52 \text{ K kg mol}^{-1}$.

Sol. The given values are:

$$W_{\text{solute}} = 18 \text{ g}$$

$$W_{\text{solvent}} = 1 \text{ kg}$$

$$K_b = 0.52 \text{ K kg mol}^{-1}$$

First we calculate elevation in the boiling point of solution.

$$\begin{aligned} \Delta T_b &= \frac{K_b \times W_{\text{solute}}}{M_{w_{\text{solute}}} \times W_{\text{solvent}}} \\ &= \frac{0.52 \times 18}{180 \times 1} = 0.052 \text{ K} \end{aligned}$$

Since water boils at 373.15 K at 1 atm pressure, therefore the boiling point of solution will be

$$T_B = T_b^\circ + \Delta T_b = 373.15 + 0.052 = 373.202 \text{ K}$$

Thus, the boiling point of solution is 373.202 K .

ILLUSTRATION 2.93

0.90 g of a non-electrolyte was dissolved in 90 g of benzene. This raised the boiling point of benzene by 0.25°C . If the molecular mass of the non-electrolyte is 100.0 g mol^{-1} , calculate the molar elevation constant for benzene.

Sol. The given values are:

$$W_{\text{solute}} = 0.90 \text{ g}$$

$$W_{\text{solvent}} = 90.00 \text{ g}$$

$$\Delta T_b = 0.25^\circ\text{C}$$

$$M_{w_{\text{solute}}} = 100.0 \text{ g mol}^{-1}$$

$$K_b = ?$$

Using the formula

$$K_b = \frac{\Delta T_b \times W_{\text{solvent}} \times M_{w_{\text{solvent}}}}{1000 \times M_{w_{\text{solute}}}}$$

$$\therefore K_b = \frac{0.25 \times 100 \times 90.0}{1000 \times 0.90} = 2.5 \text{ K m}^{-1}$$

Thus, K_b is 2.5 K m^{-1} .

ILLUSTRATION 2.94

The boiling point of benzene is 353.23 K . When 1.80 g of a non-volatile solute was dissolved in 90 g benzene, the boiling point is raised to 354.11 K . Calculate the molar mass of the solute. (K_b for benzene is $2.53 \text{ K kg mol}^{-1}$)

Sol. Given values are:

$$T_{\text{b(benzene)}}^\circ = 353.00 \text{ K}; K_b = 2.53 \text{ K kg mol}^{-1}$$

$$T_{\text{b(solution)}} = 354.00 \text{ K}$$

$$W_{\text{solute}} = 1.80 \text{ g}$$

$$W_{\text{solvent}} = 90 \text{ g}$$

$$\begin{aligned} \text{The elevation in boiling point, } \Delta T_b &= T_{\text{b(solution)}} - T_{\text{b(solvent)}}^\circ \\ &= 354.11 - 353.23 \\ &= 0.88 \text{ K} \end{aligned}$$

Molar mass of solute is given as

$$\begin{aligned} M_{w_{\text{solute}}} &= \frac{K_b \times 1000 \times W_{\text{solute}}}{\Delta T_b \times W_{\text{solvent}}} \\ M_{w_{\text{solute}}} &= \frac{2.53 \times 1000 \times 1.80}{0.88 \times 90} = 58.0 \text{ g mol}^{-1} \end{aligned}$$

Hence, the molar mass of solute is 58.0 g mol^{-1} .

ILLUSTRATION 2.95

Calculate the molar mass of a substance 1 g of which when dissolved in 100 g of water gave a solution boiling at 100.1°C at a pressure of 1 atm (K_b for water = $0.52 \text{ K kg mol}^{-1}$)

Sol. The given values are

$$W_B = 1 \text{ g}; K_b = 0.52 \text{ K kg mol}^{-1}$$

$$W_A = 100 \text{ g}$$

$$\Delta T_b = 100.1 - 100 = 0.1$$

Using the equation

$$M_{w_B} = \frac{K_b \times W_B}{\Delta T_b \times W_A}$$

Substituting all values, we get

$$\therefore M_{w_B} = \frac{0.52 \times 1 \times 1000}{0.1 \times 100} = 52$$

ILLUSTRATION 2.96

On dissolving 3.24 g of sulphur in 40 g of benzene, the boiling point of the solution was higher than that of benzene by 0.81 K. What is the molecular formula of sulphur? (K_b for benzene = 2.53 K kg mol⁻¹, atomic mass of sulphur = 32 g mol⁻¹).

Sol. The given values are:

$$W_B = 3.24 \text{ g}; \quad W_A = 40 \text{ g}$$

$$\Delta T_b = 0.81 \text{ K}; \quad K_b = 2.53 \text{ K kg mol}^{-1}$$

Using formula,

$$M_{w_B} = \frac{K_b \times 1000 \times W_B}{\Delta T_b \times W_A}$$

On substituting all the values, we get

$$\therefore M_{w_B} = \frac{2.53 \times 1000 \times 3.24}{0.81 \times 40} = 253$$

Let the molecular formula of sulphur = S_x

Atomic mass of sulphur = 32

Molecular mass = 32 × x

$$\therefore 32x = 253$$

$$x = \frac{253}{32} = 7.91 \approx 8$$

\therefore Molecular formula of sulphur = S₈

ILLUSTRATION 2.97

A solution containing 12 g of a non-electrolyte substance in 52 g of water gave boiling point elevation of 0.40 K. Calculate the molar mass of the substance. (K_b for water = 0.52 K kg mol⁻¹)

Sol. The given values are:

$$W_B = 12 \text{ g}; \quad W_A = 52 \text{ g}$$

$$\Delta T_b = 0.4 \text{ K}$$

Using the formula,

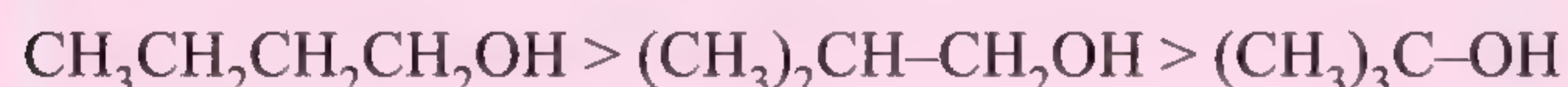
$$M_{w_B} = \frac{K_b \times W_B \times 1000}{\Delta T_b \times W_A}$$

$$\therefore M_{w_B} = \frac{0.52 \times 12 \times 1000}{0.4 \times 52} = 300$$

Molecular weight of solute is 300 g mol⁻¹.

ILLUSTRATION 2.98

Molal elevation constant (K_b) values of following alcohols are in the order:



Explain in brief.

Sol. Moving from CH₃CH₂CH₂CH₂OH to (CH₃)₃C-OH via (CH₃)₂CHCH₂OH, the branching increases, the surface area decreases resulting into decrease in van der Waal's force and hence boiling point,

$$K_b = \frac{RT_b^2 M_{w_A}}{1000 H_v}$$

molecular weight (M_{w_A}) remains the same for all three alcohols. According to Trouton's rule, $\Delta_v H/T_b$ is almost constant for all the liquids of almost similar kind of association.

Thus, $\frac{RM_{w_A} T_b}{1000 H_v}$ is constant and $K_b \propto T_b$.

2.10.3 DEPRESSION IN FREEZING POINT

We know that at freezing point of a solvent, the solid and liquid are in equilibrium. This is possible only if they have same vapour pressure. Therefore, a solution will freeze when its vapour pressure becomes equal to the vapour pressure of the pure solid solvent. Thus, the freezing point is the temperature at which the solid and liquid states of the substance have same vapour pressure. According to Raoult's law, when a non-volatile solute is added to a solvent, its vapour pressure decreases. The lower vapour pressure of a solution causes the lowering of the freezing point compared to that of the pure solvent. This may be illustrated graphically as shown in Fig. 2.19.

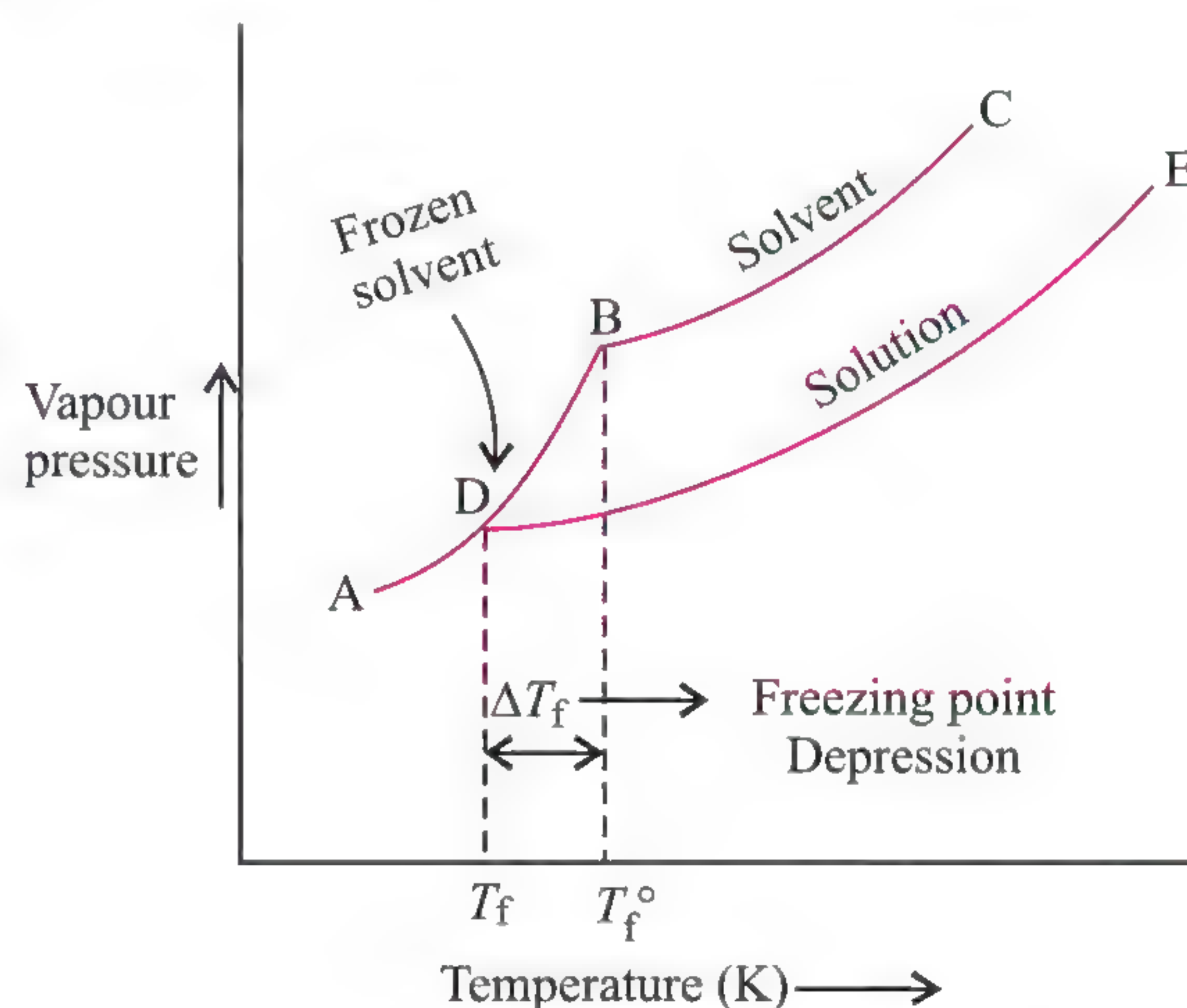


Fig. 2.19 Depression in freezing point

In the above figure, curve BC shows the variation of vapour pressure of pure solvent with temperature. The addition of non-volatile solutes lowers the vapour pressure of solvent. Curve DE shows the variations of vapour pressure of solution with temperature. Curve AB corresponds to the vapour pressure of the solid at different temperature.

Point B, where solid and liquid solvents meet (i.e., solid and liquid states have the same vapour pressure), corresponds to the temperature of freezing (T_f^0) for pure solvent. The temperature corresponding to point D where the solid solvent and liquid solution meet (i.e., solid and liquid states have the same vapour pressure) represents the freezing point temperature (T_f) of the solution.

From Fig. 2.19, it is clear that T_f is less than T_f^0 , this shows that the freezing temperature of the solution is less than that of pure solvent. The decrease in freezing point $\Delta T_f = T_f^0 - T_f$ is known as *depression in freezing point*.

Similar to the elevation in boiling point, the depression in freezing point (ΔT_f) for dilute solution is directly proportional to the molality (m) of the solution.

$$\text{Thus, } \Delta T_f \propto m \text{ or } \Delta T_f = m \times K_f \quad \dots(i)$$

The proportionality constant K_f which depends on the nature of the solvent is known as *freezing point depression constant or cryoscopic constant*. The unit of K_f is K kg mol^{-1} .

Following are the experimental methods for the determination of the depression in freezing point (ΔT_f)

- Beckmann's method
- Rast's method

DERIVATION OF THE DEPRESSION IN FREEZING POINT

The difference between the freezing points of a pure solvent and its solution is called *depression in freezing point*.

$$(\Delta T) = \text{Freezing point of the solvent} - \text{Freezing point of the solution}$$

This can be better understood by plotting a graph of vapour pressure against temperature for a pure solvent and two solutions, solution I and solution II. CFB is a curve for solid solvent. The solvent, solution I, and solution II vapour pressure curves meet CFB curve at points B, F, and C, respectively. Thus, T_0 , T_1 , and T_2 are the freezing point of pure solvent, solution I, and solution II, respectively. The solvent, solution I, and solution II are, thus, P° , P_1 , and P_2 , respectively (Fig. 2.20).

For very dilute solutions, curves FD and CE are almost straight lines and CB is also nearly a straight line. ΔBEC and ΔBDF are similar.

$$\text{So } \frac{EC}{DF} = \frac{BE}{BD}$$

$$\text{or } \frac{T_0 - T_2}{T_0 - T_1} = \frac{P^\circ - P_2}{P^\circ - P_1}$$

$$\text{or } \frac{\Delta T_2}{\Delta T_1} = \frac{\Delta P_2}{\Delta P_1} \text{ or } \Delta T \propto \Delta P$$

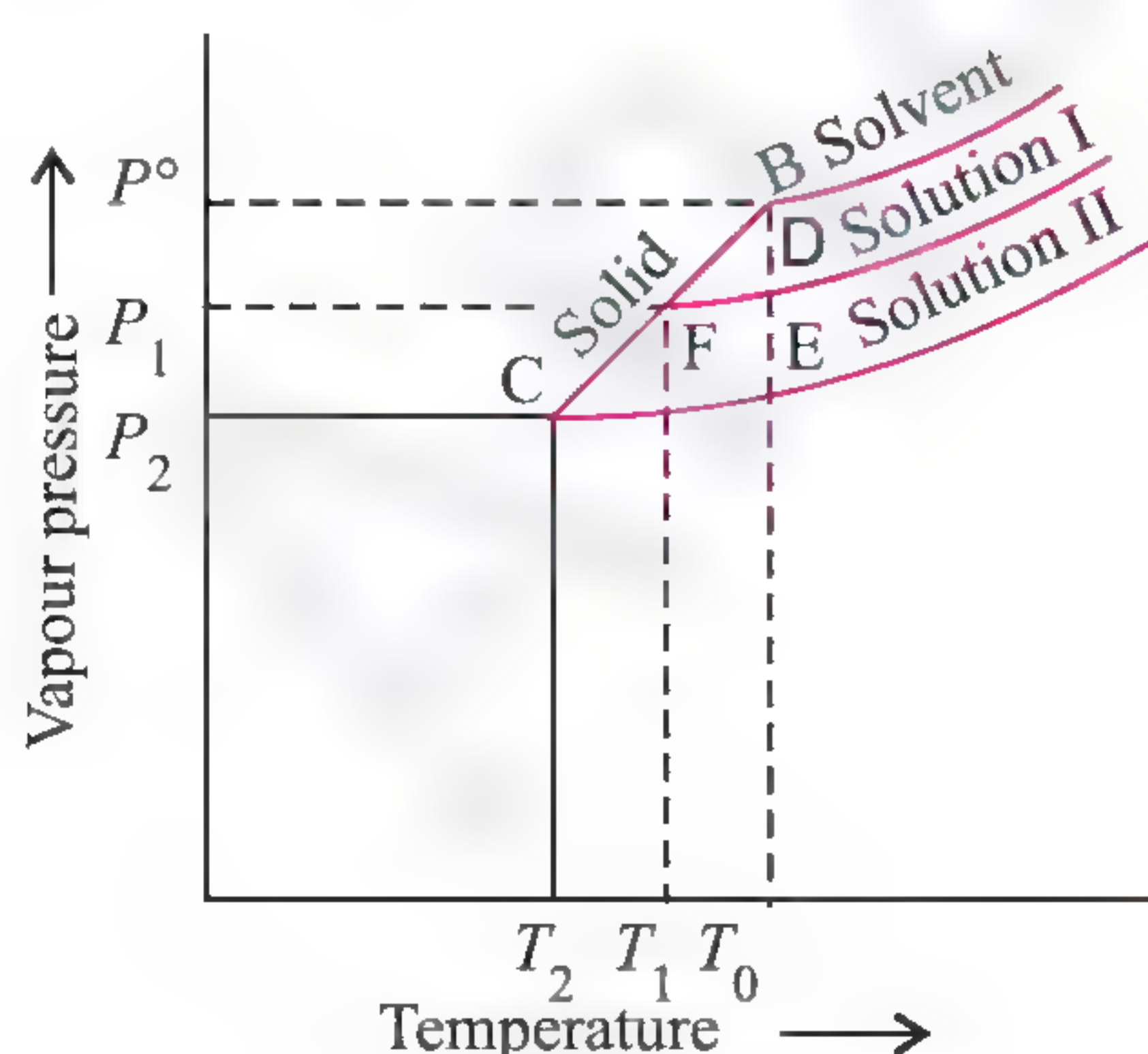


Fig. 2.20

From Raoult's law for dilute solutions,

$$\frac{P^\circ - P_s}{P^\circ} = \frac{W_B M_{wA}}{M_{wB} W_A}$$

$$\text{or } P^\circ - P_s = \frac{W_B M_{wA}}{M_{wB} W_A} P^\circ$$

For the pure solvent, P° and M_w are constant.

$$\therefore P^\circ - P_s \propto \frac{W_B}{M_{wB} \times W_A}$$

$$\text{or } \Delta P \propto \frac{W_B}{M_{wB} \times W_A}$$

$$\text{or } \Delta P \propto \Delta T \propto \frac{W_B}{M_{wB} \times W_A}$$

$$\text{or } \Delta T = K \cdot \frac{W_B}{M_{wB} \times W_A} \quad \dots(i)$$

where K is a constant called depression constant.

When $\frac{W_B}{M_{wB}} = 1$ (one mole of solute) and $W_A = 1 \text{ g}$

If $\frac{W_B}{M_{wB}} = 1$ and $W_A = 1000 \text{ g}$

$$\Delta T = \frac{K}{1000} = K_f$$

where K_f is called molal depression constant. It is defined as the depression in freezing point produced when 1 mol of solute is dissolved in 1000 g of the solvent.

Thus, $K = 1000 K_f$

Putting this value in Eq. (i), we get

$$\Delta T^* = 1000 K_f \frac{W_B}{M_{wB} W_A}$$

$$\text{or } \Delta T = \text{Molality} \times K_f$$

RELATION BETWEEN MOLAL DEPRESSION CONSTANT AND ENTHALPY OF FUSION

K_f is characteristic of a particular solvent and can be calculated from the thermodynamical relationship.

$$K_f = \frac{M_{wA} R T_f^2}{\Delta_{\text{fus}} H \times 1000} \text{ or } K_f = \frac{R T_f^2}{l_f \times 1000}$$

where M_{wA} is the molar mass of solvent, T_f is the freezing point of solvent, $\Delta_{\text{fus}} H$ is the molar enthalpy of fusion of the solvent, R is the gas constant, and l_f is the latent heat of fusion.

Determination of Depression in Freezing Point

In case of depression of freezing point determination

Case (a): When water as solvent is in excess, remaining water will separate out as ice. Refer Illustrations 2.135 and 2.136.

Case (b): When solute is in excess, remaining solute will precipitate. Refer Illustration 2.137.

ILLUSTRATION 2.99

Why is it advised to add ethylene glycol to water in car radiator while driving in a hill station?

Sol. Ethylene glycol lowers the freezing point of water, and therefore, it does not freeze in a hill station.

ILLUSTRATION 2.100

Sodium chloride solution freezes at lower temperature than water but boils at higher temperature than water. Explain.

Sol. The freezing point of a liquid depresses on the addition of a non-volatile solute, and therefore, a solution of sodium chloride freezes at a temperature lower than the freezing point of water. On the other hand, there is elevation of boiling point on the addition of a non-volatile solute and consequently the boiling point of sodium chloride solution is more than that of water.

ILLUSTRATION 2.101

Why is camphor preferred as a solvent for measuring the molecular mass of naphthalene by Rast method?

Sol. Camphor has a large K_f value (39.8°), and therefore, it causes large depression in the melting point of a solution with very small amount of solute (naphthalene).

ILLUSTRATION 2.102

Sodium chloride or calcium chloride is used to clear snow from the roads. Why?

Sol. Sodium chloride depress the freezing point of water to such an extent that it cannot freeze to form ice. Therefore, it melts off easily at the prevailing temperature.

ILLUSTRATION 2.103

Define molal depression constant or cryoscopic constant.

Sol. It is the depression in freezing point when 1 mol of a non-volatile solute is dissolved in 1000 g of a solvent.

ILLUSTRATION 2.104

What is an antifreeze?

Sol. A substance (such as ethylene glycol) which is added to water to lower its freezing point is called an antifreeze. It is so named because it delays freezing.

ILLUSTRATION 2.105

What are units of cryoscopic constant?

Sol. K kg mol^{-1} .

ILLUSTRATION 2.106

What is de-icing agent? How does it work?

Sol. Common salt is called de-icing agent as it lowers the freezing point of water to such an extent that it does not freeze to form ice. Thus, it is used to clear snow from roads.

ILLUSTRATION 2.107

What do you understand by the term that K_f for water is $1.86 \text{ K kg mol}^{-1}$?

Sol. It means that the freezing point of water is lowered by 1.86 K when 1 mol of a non-volatile solute is dissolved in 1000 g of water.

ILLUSTRATION 2.108

Calculate the molal depression constant of a solvent which has

- Freezing point 16.6°C and latent heat of fusion 180.75 J g^{-1} .
- Freezing point 20.0°C and latent heat of fusion 200.00 J g^{-1} .

Sol. a. $K_f = \frac{RT_f^2}{1000 \times l_f} \quad \dots(i)$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T_f = 16.6^\circ\text{C} = 273 + 16.6 = 289.6 \text{ K}$$

$$l_f = 180.75 \text{ J g}^{-1}$$

Substituting the values in Eq. (i), we get

$$K_f = \frac{8.314 \times (289.6)^2}{1000 \times 180.75} = 3.86$$

b. $K_f = \frac{RT_f^2}{1000 \times l_f}$

$$T_f = 273 + 20.0 = 293.0$$

$$l_f = 200.0 \text{ J g}^{-1} = \frac{8.314 \times (293.0)^2}{1000 \times 200.0} = 3.56$$

ILLUSTRATION 2.109

If the boiling point of an aqueous solution containing a non-volatile solute is 100.15°C . What is its freezing point? Given latent heat of fusion and vapourization of water 80 cal g^{-1} and 540 cal g^{-1} , respectively.

Sol. For a given aqueous solution,

$$\Delta T_f = K_f \times m \quad \dots(i)$$

$$\Delta T_b = K_b \times m \quad \dots(ii)$$

$$K_f = \frac{RT_f^2}{1000 l_f} \quad \dots(iii)$$

$$K_b = \frac{RT_b^2}{1000 l_v} \quad \dots(iv)$$

Dividing Eq. (iii) by Eq. (iv),

$$\frac{K_f}{K_b} = \frac{T_f^2 \times l_v}{T_b^2 \times l_f}$$

$$\therefore \frac{\Delta T_f}{\Delta T_b} = \frac{T_f^2 \times l_v}{T_b^2 \times l_f}$$

$$T_f = 0 + 273 = 273 \text{ K},$$

$$T_b = 100 + 273 = 373 \text{ K}$$

$$l_f = 80 \text{ cal g}^{-1}, l_v = 540 \text{ cal g}^{-1}$$

$$\therefore \frac{\Delta T_f}{0.15} = \frac{273 \times 273 \times 540}{373 \times 373 \times 80}$$

$$\text{or } \Delta T_f = \frac{273 \times 273 \times 540}{373 \times 373 \times 80} \times 0.15 = 0.542$$

$$\therefore T_f = 0 - 0.542 = -0.542^\circ\text{C}$$

ILLUSTRATION 2.110

1.4 g of acetone dissolved in 100 g of benzene gave a solution which freezes at 277.12 K. Pure benzene freezes at 278.4 K. 2.8 g of solid (A) dissolved in 100 g of benzene gave a solution which froze at 277.76 K. Calculate the molecular mass of (A).

Sol. We know that

$$\Delta T = K_f \times \frac{W_2 \times 1000}{Mw_2 \times W_1}$$

where ΔT = Depression in freezing point

K_f = Molal depression constant of benzene

W_2 = Mass of solute

Mw_2 = Molecular mass of solute

W_1 = Mass of solvent

$$\text{Case I: } (278.4 - 277.12) = K_f \times \frac{1.4 \times 1000}{58 \times 100}$$

$$1.28 = K_f \times \frac{14}{58} \quad \dots(i)$$

$$\text{Case II: } (278.4 - 277.76) = K_f \times \frac{2.8 \times 1000}{Mw_A \times 100}$$

$$0.64 = K_f \times \frac{28}{Mw_A} \quad \dots(ii)$$

Dividing Eq. (i) by Eq. (ii), we get

$$Mw_A = 232$$

ILLUSTRATION 2.111

The freezing point of a solution containing 50 cm³ of ethylene glycol in 50 g of water is found to be -34°C. Assuming ideal behaviour, calculate the density of ethylene glycol (K_f for water = 1.86 K kg mol⁻¹).

$$\text{Sol. } \Delta T = \frac{K_f \times W_2 \times 1000}{Mw_2 \times W_1}$$

$$34 = 1.86 \times \frac{W_2 \times 1000}{62 \times 50}$$

$$W_2 = 56.66 \text{ g}$$

$$V = \frac{W_2}{d}$$

$$50 = \frac{56.66}{d}$$

$$d = 1.13 \text{ g cm}^{-3}$$

ILLUSTRATION 2.112

An aqueous solution of a non-volatile solute boils at 100.17°C. At what temperature will the solution freeze? (Given: $K_b = 0.512$ and $K_f = 1.86$)

Sol. We know that

$$\Delta T_b = \text{Molality} \times K_b$$

$$0.17 = \text{Molality} \times 0.512$$

$$\text{Molality of the solution} = \frac{0.17}{0.512} \text{ m}$$

Let depression in freezing point be ΔT_f

$$\Delta T_f = \text{Molality} \times K_f$$

$$= \frac{0.17}{0.512} \times 1.86 = 0.62^\circ\text{C}$$

Thus, the freezing point of the solution is

$$0.00 - 0.62 = -0.62^\circ\text{C}$$

ILLUSTRATION 2.113

A solution of urea in water has boiling point of 100.15°C. Calculate the freezing point of the same solution if K_f and K_b for water are 1.87 K kg mol⁻¹ and 0.52 K kg mol⁻¹, respectively.

$$\text{Sol. } \Delta T_b = (100.15 - 100) = 0.15^\circ\text{C}$$

We know that $\Delta T_b = \text{Molality} \times K_b$

$$\text{Molality} = \frac{\Delta T_b}{K_b} = \frac{0.15}{0.52} = 0.2884$$

$$\Delta T_f = \text{Molality} \times K_f$$

$$= 0.2884 \times 1.87$$

$$= 0.54^\circ\text{C}$$

Thus, the freezing point of the solution = -0.54°C

ILLUSTRATION 2.114

By dissolving 13.6 g of a substance in 20 g of water, the freezing point decreased by 3.7°C. Calculate the molecular mass of the substance. (Molal depression constant for water = 1.863 K kg mol⁻¹)

$$\text{Sol. } Mw_2 = \frac{1000K_f \times W_2}{W_1 \times \Delta T}$$

Given, $K_f = 1.863 \text{ K kg mol}^{-1}$

$W_2 = 13.6 \text{ g}$, $W_1 = 20 \text{ g}$, $\Delta T = 3.7^\circ\text{C}$

$$Mw_2 = \frac{1000 \times 1.863 \times 13.6}{20 \times 3.7} = 342.39$$

ILLUSTRATION 2.115

On dissolving 0.25 g of a non-volatile substance in 30 mL benzene (density 0.8 g mL⁻¹), its freezing point decreases by 0.25°C. Calculate the molecular mass of non-volatile substance ($K_f = 5.1 \text{ K kg mol}^{-1}$).

$$\text{Sol. } \text{Mass of benzene, } W = \text{Volume} \times \text{Density} \\ = 30 \times 0.8 = 24 \text{ g}$$

Given, $K_f = 5.12 \text{ K kg mol}^{-1}$, $W_2 = 0.25 \text{ g}$

$\Delta T = 0.25^\circ\text{C}$,

We know that

$$Mw_2 = \frac{1000K_f \times W_2}{W_1 \times \Delta T} \text{ (substituting all values)}$$

$$= \frac{100 \times 5.12 \times 0.25}{24 \times 0.25} = 213.33$$

ILLUSTRATION 2.116

In a cold climate water gets frozen causing damage to radiator of a car. Ethylene glycol is used as an antifreezing agent. Calculate the amount of ethylene glycol to be added to 4 kg of water to prevent it from freezing at -6°C. (K_f for water = 1.85 K kg mol⁻¹)

Sol. Given,

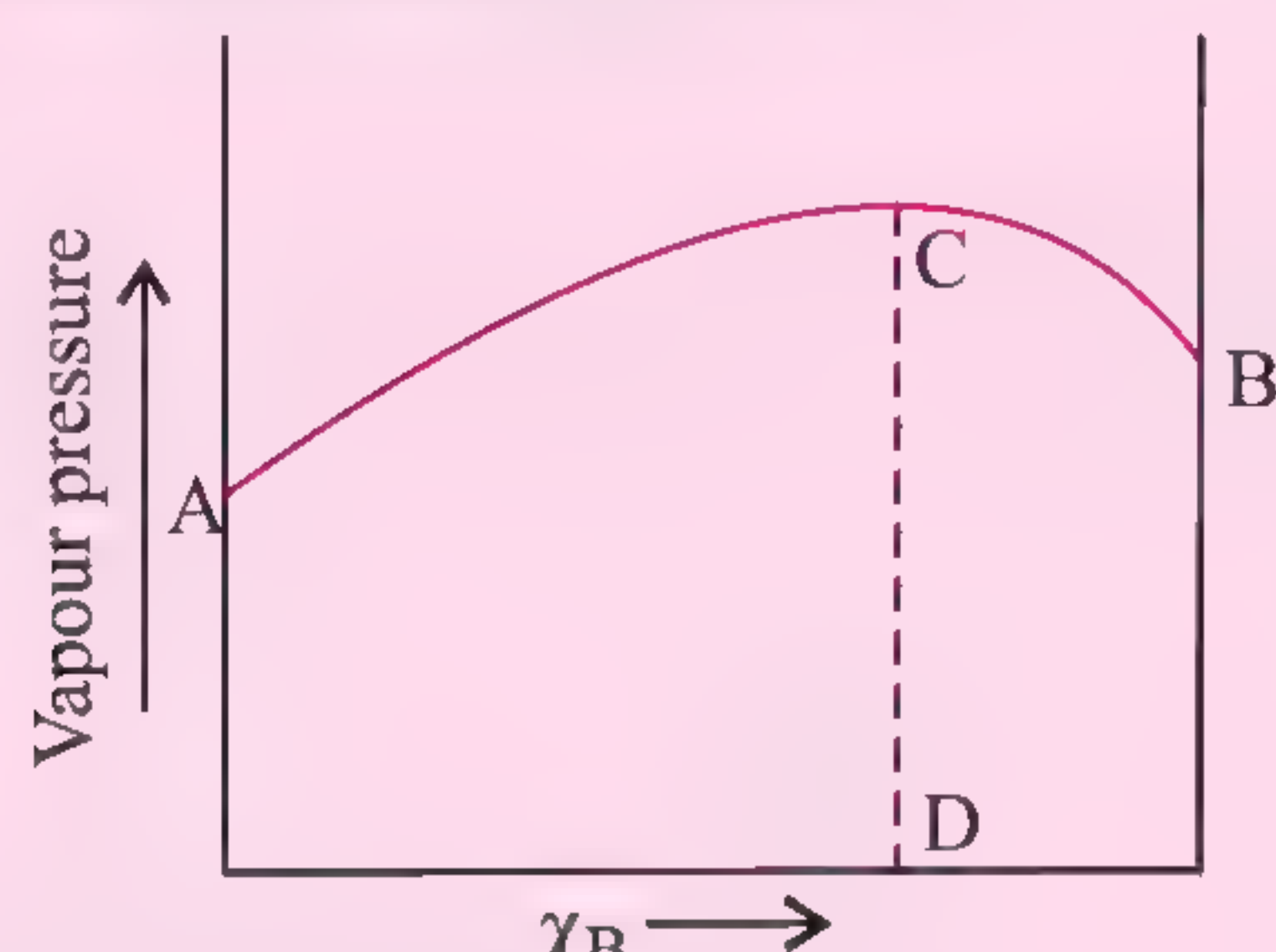
$$\Delta T = 6^\circ\text{C}, W_2 = 4 \text{ kg} = 4000 \text{ g}, Mw_2 = 62, K_f = 1.85$$

$$W_2 = \frac{Mw_2 \times W_1 \times \Delta T}{1000 \times K_f}$$

$$= \frac{62 \times 4000 \times 6}{1000 \times 1.85} = 804.32 \text{ g}$$

ILLUSTRATION 2.117

The diagram given below is a vapour-pressure-composition diagram for a binary solution of A and B.



In the solution, A–B interactions are:

- Similar to A–A and B–B interactions
- Greater than A–A and B–B interactions
- Smaller than A–A and B–B interactions
- Unpredictable

Sol. c. The solution is showing positive deviation from Raoult's law. Therefore interaction between A–A and B–B is smaller than A–B interaction.

ILLUSTRATION 2.118

1.355 g of a substance dissolved in 55 g of CH_3COOH produced a depression in the freezing point of 0.618°C . Calculate the molecular weight of the substance ($K_f = 3.85$)

Sol. $\Delta T = K_f \frac{W_B \times 1000}{Mw_B \times W_A}$

where W_B = mass of solute, Mw_B = molar mass of solute,
 W_A = mass of solvent

$$0.618 = 3.85 \times \frac{1.355 \times 1000}{Mw_B \times 55}$$

$$Mw_B = 153.47$$

ILLUSTRATION 2.119

What mass of sugar $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ($M_0 = 342$) must be dissolved in 4.0 kg of H_2O to yield a solution that will freeze at -3.72°C . (Take $K_f = 1.86^\circ\text{C m}^{-1}$)

Sol. $\Delta T_f = 3.72^\circ\text{C}$ $Mw_{\text{sugar}} = 342$

$$\Delta T_f = K_f \left[\frac{W_B \times 1000}{Mw_B \times W_A} \right]$$

$$\Rightarrow W_B = \frac{\Delta T_f W_A Mw_B}{1000 K_f}$$

$$\Rightarrow W_B = \frac{3.72 \times 4 \times 10^3 \times 342}{1000 \times 1.86} = 2736 \text{ g}$$

ILLUSTRATION 2.120

Calculate the freezing point depression and boiling point elevation of a solution of 10.0 g of urea ($M_B = 60$) in 50.0 g of water at 1 atm. pressure. K_b and K_f for water $0.52^\circ\text{C m}^{-1}$ and $1.86^\circ\text{C m}^{-1}$ respectively.

Sol. Depression in freezing point $= \Delta T_f$ and elevation in boiling point $= \Delta T_b$

$$\Delta T_f = K_f \left(\frac{W_B}{\frac{Mw_B}{W_A} \times 1000} \right) = 1.86 \left(\frac{10}{\frac{60}{50} \times 1000} \right) = 6.2^\circ\text{C}$$

$$\Delta T_b = K_b \left(\frac{W_B}{\frac{Mw_B}{W_A} \times 1000} \right) = 0.52 \left(\frac{10}{\frac{60}{50} \times 1000} \right) = 1.7^\circ\text{C}$$

$$\text{Freezing point } (T_f) = T_f^\circ - \Delta T_f = 0 - 6.2 = -6.2^\circ\text{C}$$

$$\text{Boiling point } (T_b) = T_b^\circ + \Delta T_b = 100 + 1.7 = 101.7^\circ\text{C}$$

ILLUSTRATION 2.121

1 g of monobasic acid in 100 g of water lowers the freezing point by 0.168° . If 0.2 g of same acid requires 15.1 mL mol^{-1} of N/10 alkali for complete neutralization, calculate the degree of dissociation of acid. K'_f for H_2O is $1.86 \text{ K mol}^{-1} \text{ kg}$.

Sol. $\Delta T = \frac{1000 \times K_f \times W_2}{Mw_2 \times W_1}$

and $\Delta T = 0.168$, $W_2 = 1 \text{ g}$, $W_1 = 100 \text{ g}$ and $K'_f = 1.86$

$$\therefore Mw_{\text{acid}} = 110.71 \text{ (This is exp. mol. wt.)}$$

Now, mEq of acid = mEq of alkali

$$\frac{0.2}{E} \times 1000 = 15.1 \times \frac{1}{10}$$

$$\therefore Ew \text{ of acid} = \frac{0.2 \times 1000 \times 10}{15.1} = 132.45$$

$$\therefore \text{Normal } Mw = 132.45 \times 1$$

(Since monobasic)

	$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$
Before dissociation	1 0 0
After dissociation	$(1 - \alpha)$ α α

$$\text{Now, } \frac{Mw_{\text{Normal}}}{Mw_{\text{Exp}}} = \frac{132.45}{110.71} = 1 + \alpha \Rightarrow \alpha = 19.6\%$$

ILLUSTRATION 2.122

How many grams of sucrose (molecular weight 342) should be dissolved in 100 g water in order to produce a solution with 105°C difference between the freezing point and the boiling point? ($K_b = 0.51^\circ\text{C m}^{-1}$, $K_f = 1.86^\circ\text{C m}^{-1}$)

Sol. The given values are

$$W_{\text{solvent}} = 100 \text{ g}$$

$$Mw_{\text{solute}} = 342 \text{ g mol}^{-1}$$

$$T_b - T_f = 105.0^\circ\text{C}$$

Using the formula, $\Delta T_b = K_b m$ and $\Delta T_f = K_f m$

$$\begin{aligned}\text{Boiling point of solution } (T_b) &= 100 + \Delta T_b \\ &= 100 + K_b m \quad \dots(i)\end{aligned}$$

$$\begin{aligned}\text{Freezing point of solution } (T_f) &= 0 - \Delta T_f \\ &= 0 - K_f m \quad \dots(ii)\end{aligned}$$

Subtracting Eq. (ii) from Eq. (i),

$$T_b - T_f = (100 + K_b m) - (-K_f m)$$

$$105 = 100 + 0.51m + 1.86m$$

$$m = 2.11$$

Weight of sucrose to be dissolved in 100 g

$$= \frac{2.11 \times 342 \times 100}{1000} = 72.16 \text{ g}$$

ILLUSTRATION 2.123

A liquid possessing which of the following characteristics will be most suitable for determining the molecular mass of a compound by cryoscopic measurements?

- That having low freezing point and small enthalpy of fusion
- That having high freezing point and small enthalpy of fusion
- That having high freezing point and small enthalpy of vapourization
- That having large surface tension

Sol. b. K_f should be high so as to get a high value of ΔT_f .

$$\text{Now } K_f \propto \frac{T_f^2}{\Delta_{\text{vap}} H}$$

ILLUSTRATION 2.124

45 g of ethylene glycol $\text{C}_2\text{H}_6\text{O}_2$ is mixed with 600 g of water. Calculate (a) the freezing point depression and (b) the freezing point of the solution.

Given $K_f = 1.86 \text{ K kg mol}^{-1}$.

Sol. Depression in freezing point is related to the molality, therefore the molality of the solution with respect to ethylene glycol,

$$\Delta T_f = K_f m$$

$$\text{Mole of ethylene glycol} = 45 \text{ g} \times \frac{1 \text{ mol}}{62 \text{ g}} = 0.73 \text{ mol}$$

$$\text{Mass of water in kg} = 600 \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.60 \text{ kg}$$

Hence, molality of ethylene glycol

$$= \frac{0.73 \text{ mol}}{0.60 \text{ kg}} = 1.20 \text{ mol kg}^{-1}$$

Therefore, freezing point depression

$$\Delta T_f = 1.86 \text{ K kg mol}^{-1} \times 1.2 \text{ mol kg}^{-1} = 2.2 \text{ K}$$

Freezing point of the aqueous solution

$$\begin{aligned}T_f &= T_f^\circ - \Delta_f T \\ &= 273.15 \text{ K} - 2.2 \text{ K} = 270.95 \text{ K}\end{aligned}$$

ILLUSTRATION 2.125

1.0 g of non-electrolyte solute dissolved in 50.0 g of benzene lowered the freezing point of benzene by 0.40 K. The freezing point depression constant of benzene is $5.12 \text{ K kg mol}^{-1}$. Find the molecular mass of the solute.

Sol. Given values are:

$$W_{\text{solute}} = 1.0 \text{ g}$$

$$W_{\text{solvent}} = 50.0 \text{ g}$$

$$\Delta T_f = 0.40 \text{ K}$$

$$K_f = 5.12 \text{ K kg mol}^{-1}$$

Substituting this value in equation

$$\begin{aligned}M_{W_{\text{solute}}} &= \frac{K_f \times W_{\text{solute}} \times 1000}{\Delta T_f \times W_{\text{solvent}}} \\ &= \frac{5.12 \text{ K kg mol}^{-1} \times 1.0 \times 1000}{0.40 \text{ K} \times 50.0 \text{ g}} \\ &= 256.0 \text{ g mol}^{-1}\end{aligned}$$

Thus, molecular mass of the solute = 256.0 g mol^{-1}

ILLUSTRATION 2.126

Addition of 0.40 g of a compound to 45.5 mL of benzene (density 0.879 g mL^{-1}) lowers the freezing point from 5.51°C to 4.998°C . If K_f for benzene is $5.12 \text{ K kg mol}^{-1}$, calculate the molar mass of the compound.

Sol. The given values are:

$$W_{\text{solute}} = 0.40 \text{ g}; K_f = 5.12 \text{ K m}^{-1}$$

$$\rho_{(\text{benzene})} = 0.879 \text{ g mL}^{-1}$$

$$V_{(\text{benzene})} = 45.50 \text{ mL}$$

$$\Delta T_f = T_f^\circ - T_f = 5.51 - 5.03 = 0.512^\circ\text{C}$$

Now weight of benzene = $V \times \rho$

$$= 45.50 \times 0.879$$

$$= 40.00 \text{ g}$$

Molar mass of solute, M_{solute} is calculated as

$$\begin{aligned}M_{W_{\text{solute}}} &= \frac{K_f \times W_{\text{solute}} \times 1000}{W_{\text{solvent}} \times \Delta T_f} \\ &= \frac{5.12 \times 0.40 \times 1000}{40 \times 0.512} = 400\end{aligned}$$

Thus, the molecular weight of solute is 400 g mol^{-1} .

ILLUSTRATION 2.127

The molal freezing point depression constant of benzene (C_6H_6) is $4.90 \text{ K kg mol}^{-1}$. Selenium exists as a polymer of the type Se_x . When 3.26 g of selenium is dissolved in 226 g of benzene, the observed freezing point is 0.112°C lower than pure benzene. Deduce the molecular formula of selenium. (Atomic mass of $\text{Se} = 78.8 \text{ g mol}^{-1}$)

Sol. The given values are:

$$K_f = 4.90 \text{ K kg mol}^{-1}$$

$$W_{\text{solute}} = 3.26 \text{ g}$$

$$W_{\text{solvent}} = 226 \text{ g}$$

$$\Delta T_f = 0.112^\circ\text{C}$$

Now, molecular mass can be calculated as

$$\begin{aligned} M_{w_{\text{solute}}} &= \frac{K_f \times W_{\text{solute}} \times 1000}{W_{\text{solvent}} \times \Delta T_f} \\ &= \frac{4.901 \times 3.26 \times 1000}{226 \times 0.112} = 632 \text{ g mol}^{-1} \end{aligned}$$

Now, molecular mass of $\text{Se}_x = x \times 78.8$

$$632 = x \times 78.8$$

$$\text{or } x = \frac{632}{78.8} = 8$$

\therefore Molecular formula of selenium = Se_8 .

ILLUSTRATION 2.128

Two elements A and B form compounds having molecular formula AB_2 and AB_4 . When dissolved in 20 g of benzene, 1 g of AB_2 lowers the freezing point by 2.3 K, whereas 1.0 g of AB_4 lowers it by 1.3 K. The molar depression constant for benzene is $5.1 \text{ K kg mol}^{-1}$. Calculate the atomic mass of A and B.

Sol. Given values are:

$$W_{\text{AB}_2} = 1.0 \text{ g}; W_{\text{benzene}} = 20 \text{ g}$$

$$W_{\text{AB}_4} = 1.0 \text{ g}$$

$$\Delta T_{f(\text{AB}_2)} = 2.3 \text{ K}$$

$$\Delta T_{f(\text{AB}_4)} = 1.3 \text{ K}$$

Let us calculate the molar masses of AB_2 and AB_4 .

For AB_2 compound

$$M_{w_{\text{solute}}} = \frac{K_f \times W_{\text{solute}} \times 1000}{W_{\text{solvent}} \times \Delta T_f}$$

$$M_{w_{\text{AB}_2}} = \frac{5.1 \times 1.0 \times 1000}{20.0 \times 2.3} = 110.87 \text{ g mol}^{-1}$$

$$\therefore M_{w_{\text{AB}_2}} = 110.87 \text{ g mol}^{-1}$$

For AB_4 compound

$$M_{w_{\text{AB}_4}} = \frac{5.1 \times 1.0 \times 1000}{20.0 \times 1.3} = 196.15 \text{ g mol}^{-1}$$

Let α is the atomic mass of A and β is the atomic mass of B, then

$$M_{w_{\text{AB}_2}} = \alpha + 2\beta = 110.87 \quad \dots(i)$$

$$M_{w_{\text{AB}_4}} = \alpha + 4\beta = 196.15 \quad \dots(ii)$$

Subtracting Eq. (ii) from Eq. (i), we get

$$-2\beta = -85.28$$

$$\therefore \beta = 42.64$$

Substituting the value of β in Eq. (i),

$$\alpha + 2 \times 42.64 = 110.87$$

$$\alpha = 110.87 - 85.28 = 25.59$$

$$\text{Atomic mass of A} = 25.59$$

$$\text{Atomic mass of B} = 42.64$$

ILLUSTRATION 2.129

In a cold climate water gets frozen causing damages to the radiator of a car. Ethylene glycol is used as an antifreezing agent. Calculate the amount of ethylene glycol the added to 2 kg of water to prevent it from freezing at -8°C . (K_f for water = 1.8 K m^{-1})

Sol. The given values are

$$W_A = 2 \text{ kg} = 2 \times 10^3 \text{ g}; M_{w_B} = 62 \text{ g mol}^{-1}$$

$$K_f = 1.8 \text{ K m}^{-1}$$

$$\Delta T_f = 0 - (-8) = 8^\circ$$

$$\text{Using formula, } W_B = \frac{\Delta T_f \times W_A \times M_{w_B}}{K_f \times 1000}$$

$$\therefore W_B = \frac{8 \times 2 \times 10^3 \times 62}{1.8 \times 1000} = 551.1 \text{ g}$$

Therefore, the amount of ethylene glycol to be added is 551.11 g.

ILLUSTRATION 2.130

Two aqueous solution containing, respectively, 7 g urea (molar mass = 60 g) and 42 g of substance X in 100 g of water freeze at the same temperature. Calculate the molecular weight of X.

Sol. The given values are

$$W_{\text{urea}} = 7 \text{ g}$$

$$W_X = 42 \text{ g}$$

$$W_A = 100 \text{ g}$$

$$\text{Now using formula, } M_{w_B} = \frac{K_f \times W_B \times 1000}{\Delta T_f \times W_A}$$

$$\text{For urea, } M_{w_B} = \frac{K_f \times 7 \times 1000}{\Delta T_f \times 100} = 60 \quad \dots(i)$$

$$\text{For X } M_{w'_B} = \frac{K_f \times 42 \times 1000}{\Delta T_f \times 1000} \quad \dots(ii)$$

Dividing Eq. (i) from Eq. (ii), we get

$$\frac{60}{M_{w'_B}} = \frac{7}{42} \text{ or } M_{w'_B} = 360$$

$$\therefore \text{Molecular weight of X} = 360 \text{ g mol}^{-1}$$

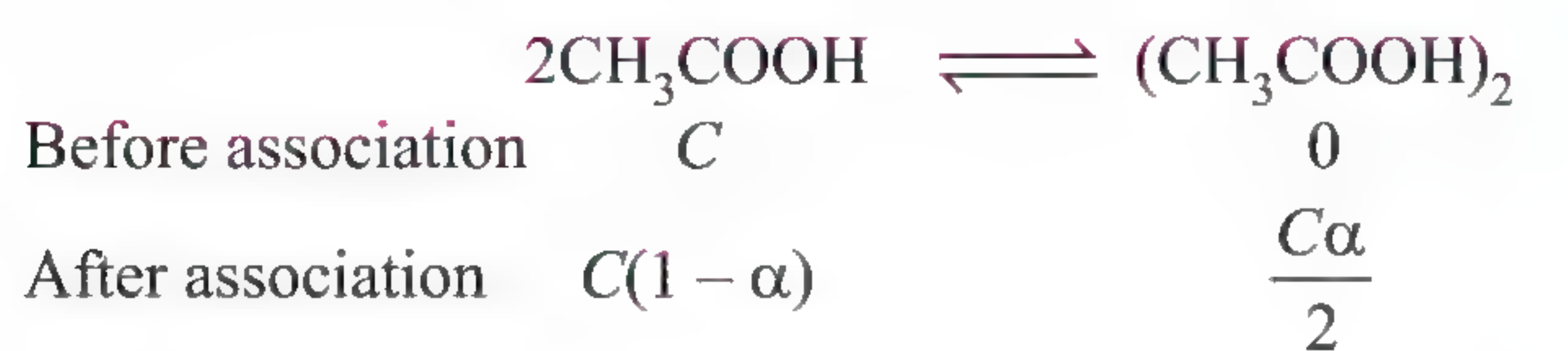
ILLUSTRATION 2.131

The freezing point of 0.02 mole fraction acetic acid in benzene is 277.4 K. Acetic acid exists partly as dimer. Calculate the equilibrium constant for dimerization. The freezing point of benzene is 278.4 K and the heat of fusion of benzene is $10.042 \text{ kJ mol}^{-1}$. Assume molarity and molality same.

$$\begin{aligned} \text{Sol. For benzene, } K'_f &= \frac{RT^2}{1000l_f (\text{cal g}^{-1})} \\ &= \frac{8.314 \times (278.4)^2}{1000 \times \frac{10.042 \times 10^3}{78}} = 5.0 \text{ K molality} \end{aligned}$$

Also,

For acetic acid in benzene



$$\therefore K_C = \frac{2}{C^2(1-\alpha)^2}$$

where α is the degree of association. ... (i)

$$\text{Also } \Delta T = K'_f \times \text{molality} \times \left(1 - \frac{\alpha}{2}\right) \quad \dots (ii)$$

$$\left(\because \text{Total particles at equilibrium} = 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2} \right)$$

$$\text{Given mole fraction of acetic acid} = 0.02 = \frac{n_2}{n_2 + n_1}$$

$$\therefore \text{Mole fraction of benzene} = 0.98 = \frac{n_1}{n_1 + n_2}$$

$$\frac{n_2}{n_1} = \frac{0.02}{0.98}$$

$$\therefore \text{Molality} = \frac{n_2}{W_1} \times 1000$$

$$= \frac{n_2 \times 1000}{n_1 \times M_{W_1}} = \frac{0.02 \times 1000}{0.98 \times 78} = 0.262 \text{ m}$$

$$\therefore \text{From Eq. (ii), } 1 = 5 \times 0.262 \times \left(1 - \frac{\alpha}{2}\right)$$

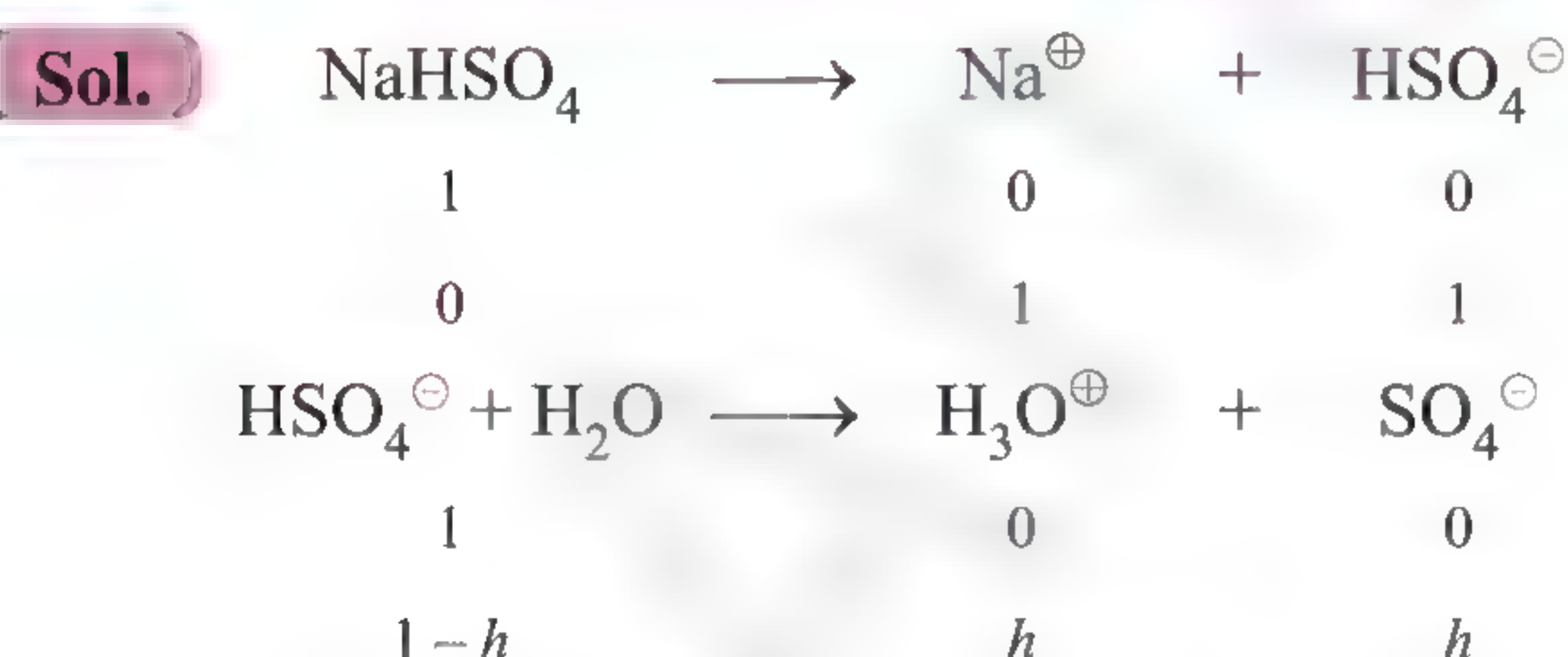
$$\therefore \alpha = 0.48$$

From Eq. (i), assuming molarity = molality

$$K_C = \frac{0.262 \times 0.48}{2 \times (0.262)^2 \times (1 - 0.48)^2} = 3.39$$

ILLUSTRATION 2.132

The freezing point of 0.08 molal NaHSO_4 is -0.345°C . Calculate the percentage of HSO_4^\ominus ions that transfers a proton to water. Assume 100% ionization of NaHSO_4 and K_f for $\text{H}_2\text{O} = 1.86 \text{ K molality}^{-1}$.



$$\therefore \text{Total particles after dissolution of NaHSO}_4 = 1 + 1 - h + h + h = 2 + h$$

$$\text{Now, } \Delta T_f = K_f \times \text{molality} \times (2 + h)$$

$$0.345 = 1.86 \times 0.08 \times (2 + h)$$

$$\therefore 2 + h = 2.319$$

$$\therefore h = 0.319$$

i.e., 31.9 % of HSO_4^\ominus shows proton transfer to H_2O .

ILLUSTRATION 2.133

Given that the latent heat of fusion of naphthalene is 19.0 kJ mol^{-1} and its melting point is 80.2°C . Estimate the solubility of naphthalene in benzene at 76.2°C .

Sol. Given

$$T^\circ = 80.2^\circ\text{C}; T_s = 76.2^\circ\text{C}$$

$$\Delta_{\text{fus}} H = 90.0 \text{ kJ mol}^{-1}$$

For an ideal solution

$$\log \chi_2 = \frac{\Delta H}{2.303R(T^\circ)^2} (T_s - T^\circ) \quad \dots (i)$$

$$\Delta H = 19000 \text{ J}, T_s - T^\circ = -4^\circ\text{C},$$

$$R = 8.314$$

Substituting all values in Eq. (i),

$$\log \chi_2 = \frac{19000}{8.314 \times 2.303 \times (353.20)^2} \times (-4)$$

$$\text{or } \chi_2 = 0.929 \approx 0.9$$

ILLUSTRATION 2.134

If a solution containing 6 g of triphenyl methane, $(\text{C}_6\text{H}_5)_3\text{CH}$ (molecular weight = 244), in 1000 g of benzene is cooled to 0.22°C below the freezing point of benzene, how much solvent will crystallize out and what will be the molality of residual solution? ($K_f = 5.1 \text{ K m}^{-1}$)

Sol. If the weight of benzene remaining as a liquid be W_1 g and

assuming triphenyl methane to be soluble in liquid benzene,

$$\Delta T_f = K_f \times m \quad \Delta T_f = 0.22, \quad K_f = 5.1 \text{ K m}^{-1}$$

$$0.22 = 5.1 \times m$$

$$m = 0.0431372 = 0.043$$

$$m = \frac{W_2 \times 1000}{M_{W_2} \times W_1}$$

$$0.043 = \frac{6 \times 1000}{244 \times W_1} \Rightarrow W_1 = 571.86 \text{ g}$$

Amount of benzene crystallizing out

$$= 1000 - 571.16 = 428.14 \text{ g}$$

ILLUSTRATION 2.135

A very small amount of a non-volatile solute (that does not dissociate) is dissolved in 56.8 cm^3 of benzene (density 0.889 g cm^{-3}). At room temperature, vapour pressure of this solution is 98.88 mm Hg while that of benzene is 100 mm Hg . Find the molality of this solution. If the freezing temperature of this solution is 0.73 degree lower than that of benzene, what is the value of molal the freezing point depression constant of benzene?

Sol. Using Raoult's law $P_1 = \chi_1 P_1^\circ$

$$\text{We get } (98.88 \text{ mm Hg}) = \chi_1 (100 \text{ mm Hg})$$

$$\text{or } \chi_1 = 0.9888$$

Let 1 mol be the total amount of solvent and solute. We will have

$$n_1 = 0.9888 \text{ mol} \quad n_2 = 0.0112 \text{ mol}$$

$$W_1 = n_1 M_{w_1} = (0.9888 \text{ mol}) (78 \text{ g mol}^{-1}) = 77.126 \text{ g}$$

The molality of the solution is

$$m = \frac{n_2}{W_1} = \frac{0.0112 \text{ mol}}{77.126 \times 10^{-3} \text{ kg}} = 0.1452 \text{ mol kg}^{-1}$$

Molal freezing point depression constant of benzene would be

$$K_f = \frac{-\Delta T_f}{m} = \frac{0.73 \text{ K}}{0.1452 \text{ mol kg}^{-1}} = 5.028 \text{ K kg mol}^{-1}$$

Questions based on when excess of solvent e.g., H₂O is taken which separates out as ice on cooling

ILLUSTRATION 2.136

Calculate the amount of ice that will separate out on cooling containing 50 g of ethylene glycol in 200 g of water to -9.3°C . (K_f for water = 1.86 K m^{-1})

Sol. Here mass of solute = 50 g

$$\Delta T_f = 9.3^\circ; K_f = 1.86 \text{ K m}^{-1} \text{ kg}$$

Molecular mass of solute $(\text{CH}_2\text{OH})_2$, $M_{w_2} = 62$

We have to calculate the mass of water in which the given mass of solute will dissolve. The rest of water will freeze out as ice. Applying the relation

$$M_{w_2} = \frac{1000 \cdot K_f \cdot W_2}{W_1 \cdot \Delta T_f}$$

$$W_1 = \frac{1000 \cdot K_f \cdot W_2}{M_{w_2} \cdot \Delta T_f} = \frac{1000 \times 1.86 \times 50}{62 \times 9.3} = 161.3 \text{ g}$$

Ice that will separate out = $200 - 161.3 = 38.7 \text{ g}$.

ILLUSTRATION 2.137

1000 g of 1 molal aqueous solution of sucrose is cooled and maintained at -3.534°C . Find out how much ice will separate out at this temperature. (K_f for water = 1.86 K m^{-1} .)

Sol. 342 g in 1000 g of H₂O = 1 m

Weight of solution = 1342 g

1342 g contains = 1000 g of H₂O

$$1000 \text{ g contains} = \frac{1000}{1342} \times 1000 = 745.156 \text{ g of H}_2\text{O}$$

Let x g of water remains in liquid state.

x g of H₂O dissolves in 1 mol solute.

$$745.15 \text{ g of H}_2\text{O dissolves} = \frac{1}{x} \times 745.156 \text{ mol of solute}$$

$$\Delta T_f = K_f \times m$$

$$3.534 = 1.86 \times \frac{745.156}{x}$$

$$x = 392.18 \text{ g}$$

Amount of water separates as ice

$$= 745.156 - 392.18$$

$$= 352.98 \text{ g}$$

Alternate method

1 m = 342 g per 1000 g of H₂O

Find sugar in 1000 g of solution.

$$1342 \text{ g solution} = 342 \text{ g sugar}$$

$$1000 \text{ g solution} = \frac{342 \times 1000}{1342}$$

$$= 254.85 \text{ g}$$

$$\text{Mass of H}_2\text{O per 1000 g solution} = 1000 - 254.85$$

$$= 745.15 \text{ g}$$

$$\Delta T_f = \frac{K_f \times 1000 \times \text{grams of sucrose}}{M_{w_{\text{sugar}}} \times \text{grams of H}_2\text{O left}}$$

$$= \frac{K_f \times W_2 \times 1000}{M_{w_2} \times W_1}$$

$$W_1 = \frac{K_f \times W_2 \times 1000}{\Delta T_f \times M_{w_2}}$$

$$= \frac{1.86 \times 254.84 \times 1000}{3.534 \times 342}$$

$$= 392.2 \text{ g H}_2\text{O}$$

$$\text{Ice separates out} = 745.15 - 392.2$$

$$= 352.95 \text{ g}$$

Questions based on when excess of solute is taken which separates out on cooling

ILLUSTRATION 2.138

A 10 m solution of urea is cooled to -13.02°C . What amount of urea will separate out if the mass of solution taken is 100 g? [K_f (water) = 1.86 K m^{-1}]

Sol. $\Delta T_f = 0 - (-13.02) = 13.02 \text{ K}$

$$m = \Delta T_f / K_f$$

$$\therefore m = \frac{13.02}{1.86} = 7.0 \text{ mol kg}^{-1}$$

$$\therefore m = 10 = \frac{W_2 \times 1000}{60 \times (100 - W_2)}$$

$$\therefore W_2 = 37.5 \text{ g}$$

Mass of H₂O in this solution = $(100 - 37.5) = 62.5 \text{ g}$

The mass of water does not change as urea separates out to bring down the molality to 7 mol kg⁻¹.

$$\therefore m = \frac{W_2 \times 1000}{M_{w_2} \times W_1}$$

$$\therefore 7 = \frac{W_2 \times 1000}{60 \times 62.5} \Rightarrow W_2 = 26.25 \text{ g}$$

$$\text{Mass of urea separated} = (37.5 - 26.25) = 11.25 \text{ g}$$

ILLUSTRATION 2.139

The melting point of phenol is 40°C . A solution containing 0.172 g acetanilide ($\text{C}_8\text{H}_9\text{OH}$) in 12.54 g phenol freezes at 39.25°C . Calculate the freezing point constant and the latent heat of fusion of phenol.

Sol. $\Delta T_f = 40 - 39.25 = 0.75$, $M_{w_2} = 135$

$$K_f = \frac{\Delta T_f}{m} = \frac{0.75}{\frac{0.172}{135} \times \frac{1000}{12.54}} = 0.738 \text{ K kg m}^{-1}$$

$$= 7.38 \text{ per } 100 \text{ g}$$

$$T_f = 273 + 40 = 313 \text{ K}$$

$$K_f = \frac{RT_f^2}{l \times 1000} = \frac{2 \times (313)^2}{l \times 1000}$$

$$l = \frac{2 \times (313)^2}{K_f \times 1000} = \frac{2 \times (313)^2}{7.38 \times 1000} = 26.5 \text{ cal g}^{-1}$$

ILLUSTRATION 2.140

How much ethyl alcohol must be added to 1.00 L of water so that the solution will not freeze at -4°F ?

Sol. Using relation

$$\Delta T_f = K_f m$$

$$\text{where } \Delta T_f = -4^{\circ}\text{F}$$

$$\text{or } -4^{\circ}\text{F} = -20^{\circ}\text{C} \quad \left[^{\circ}\text{C} = \frac{5}{9} (^{\circ}\text{F} - 32) \right]$$

$$\therefore m = \frac{\Delta T_f}{K_f} = \frac{20}{1.86} = 10.7$$

Therefore, amount of ethyl alcohol to be added

$$= m \times \text{molecular weight}$$

$$= 10.7 \times 46.0$$

$$= 495 \text{ g}$$

outer skin of the animals and plants. The pig's bladder is the most common animal membrane used.

- b. Artificial semi-permeable membranes:** Well-known examples of artificial semi-permeable membranes are parchment paper, cellophane, and certain freshly precipitated inorganic substances, e.g., copper ferrocyanide, silicates of iron, cobalt, nickel, silicates of iron, cobalt, nickel, copper ferrocyanide, etc. The precipitated substances have to be supported on some material and this is achieved by preparing the precipitate on the walls of a porous pot.

Osmosis

If we place a semi-permeable membrane between the solvent and solution as shown in Fig. 2.21 assuming that only solvent molecules can pass through these membrane, the solvent molecules will flow through the membrane from pure solvent side to the solution side. This flow of solvent from a region of higher concentration (i.e., pure solvent) to a region of lower concentration (i.e., solution) of solvent molecules is known as the phenomenon of osmosis. The phenomenon of osmosis was studied for the first time by Abbe Nollet in 1748.

As a result of osmosis, the level of solution in the tube rises, whereas that of the pure solvent falls. After some time an equilibrium is reached where the level of the solution in the tube does not rise further. At this stage, the excessive hydrostatic pressure created on the solution side exactly balances the tendency of the solvent to pass through the membrane as shown in Fig. 2.21(b). This excessive hydrostatic pressure is known as the osmotic pressure of the solution and is represented by symbol π . Thus, osmotic pressure may be defined as the excess pressure which must be applied to a solution to prevent the passage of solvent into it through a semi-permeable membrane.

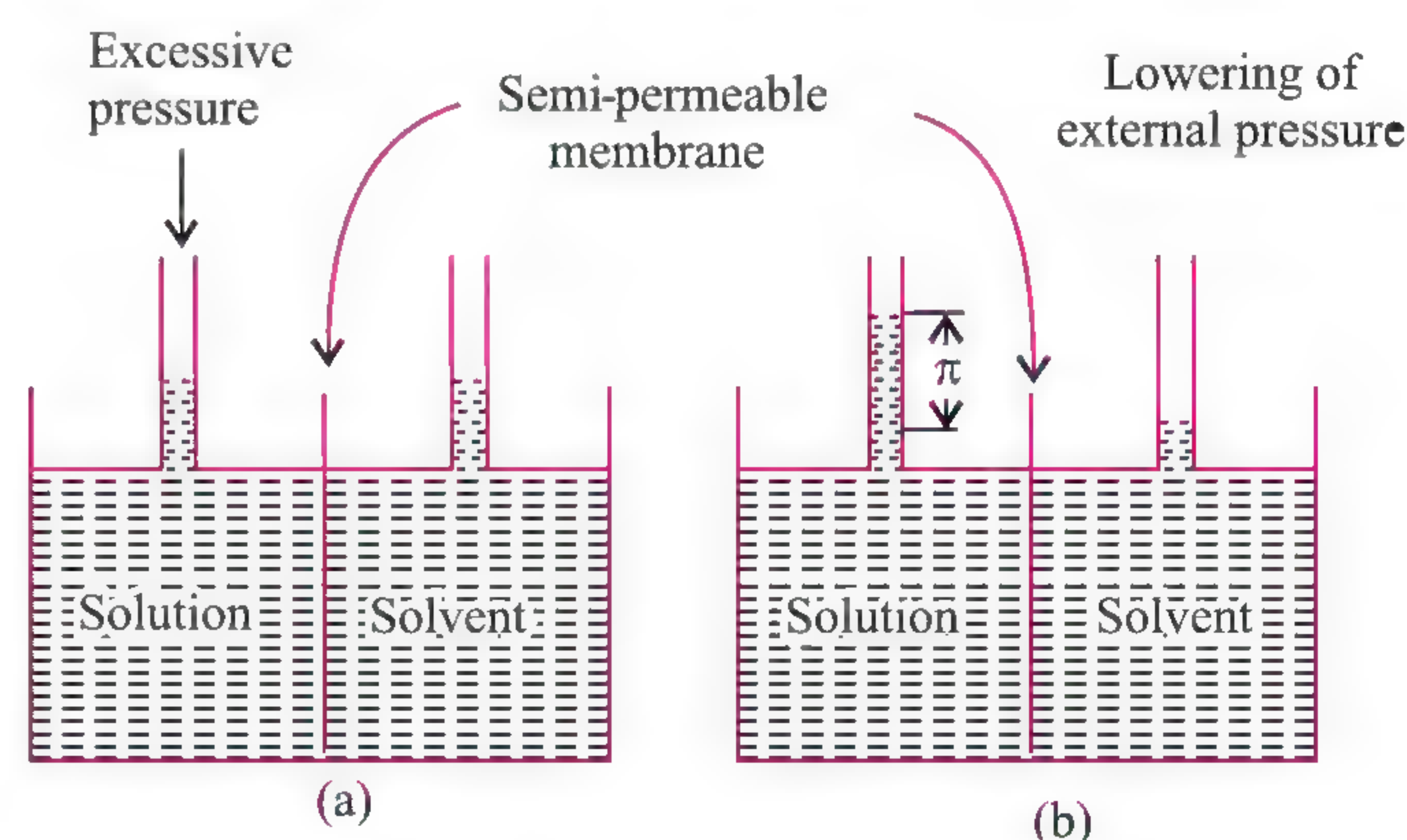


Fig. 2.21 Osmotic pressure of the solution

Osmosis can also take place between the solutions of different concentrations. In such cases, the solvent molecules move from the solution of low solute concentration to that of higher solute concentration.

The phenomenon of osmosis can be checked by increasing the external pressure on the solution by an amount equivalent to the hydrostatic pressure as shown in Fig. 2.21(b). Alternatively, this can also be checked by reducing the external pressure on the solvent side by an amount equivalent to the hydrostatic pressure.

2.10.4 OSMOSIS AND OSMOTIC PRESSURE

In nature we observe many phenomena, e.g., wilted flowers revive when placed in fresh water, blood cells get ruptured when placed in brine (salt water). In all these natural phenomena we find one common, thing that is, all these substances are bound by membranes. These membranes can be of animal or vegetable origin and these occur naturally such as pig's bladder or parchment or can be synthetic such as cellophane. These membranes appear to be continuous sheets or films. Yet they contain a network of submicroscopic holes or pores. Small solvent molecules, such as water, can pass through these holes but the passage of bigger molecules such as solutes is hindered. Membrane having this kind of properties are known as *semi-permeable membranes*. In laboratory these type of membranes are not useful because of their imperfect nature. Consequently, they can be even artificially prepared. One such membrane is the film of gelatinous precipitate of cupric ferrocyanide, $\text{Cu}_2[\text{Fe}(\text{CN})_6]$.

Semi-permeable membranes: These are of two types:

- a. Natural semi-permeable membranes:** Membranes such as animal and vegetable membranes are found just under the

Difference Between Osmosis and Diffusion

Diffusion and osmosis both involve the movement of the molecules, still they differ in the following respects:

Osmosis	Diffusion
<p>a. The process of osmosis takes place through a semi-permeable membrane.</p> <p>b. The osmosis involves the movement of the solvent molecules only.</p> <p>c. In osmosis, molecules of solvent move from a region of lower concentration of solution into a region of higher concentration.</p> <p>d. Osmosis is limited to liquid solutions only.</p> <p>e. Osmosis can be stopped or reversed by applying additional pressure on the higher concentration side.</p>	<p>a. No semi-permeable membrane is needed for the diffusion process.</p> <p>b. In diffusion both the solute and solvent molecules can move.</p> <p>c. In diffusion, the molecules move from a region of higher concentration to a region of lower concentration.</p> <p>d. Diffusion is common in gases as well as in liquids.</p> <p>e. It cannot be stopped or reversed.</p>

Osmotic Pressure: A Colligative Property

The osmotic pressure of a solution depends on its concentration—larger the concentration larger the osmotic pressure.

Van't Hoff (1887) made a thorough study of the osmotic pressure of the dilute or ideal solution. He concluded that a dilute or ideal solution behaves like an ideal gas and the different gas laws are applicable to the dilute solution as well. Van't Hoff observed that for dilute solutions, the osmotic pressure (π) is proportional to the molarity, C of the solution at a given temperature T .

$$\text{Thus, } \pi = CRT \quad \dots(i)$$

Here π is the osmotic pressure and R is the gas constant. Equation (i) is known as the *van't Hoff equation* for osmotic pressure of the solution.

The determination of the molar mass of solute includes following steps:

According to the Van't Hoff equation,

$$\pi = CRT$$

But $C = \frac{n_B}{V}$, where V is the volume of a solution in litres containing n_B moles of solute.

$$\therefore \pi = \frac{n_B}{V} RT \quad \dots(ii)$$

If W_B grams of solute of molar mass; M_{w_B} is present in the solution, then $n_B = \frac{W_B}{M_{w_B}}$

$$\pi V = \frac{W_B RT}{M_{w_B}} \quad \dots(iii)$$

$$\text{or } M_{w_B} = \frac{W_B RT}{\pi V} \quad \dots(iv)$$

Thus, knowing the quantities W_B , T , π , and V , we can calculate the molar mass of the solute.

The principal application of osmotic pressure measurement is in the determination of the molar mass of a substance which is either slightly soluble or has a very higher molar mass such as proteins, polymer of various types, and colloid. The osmotic pressure method has the advantage over other methods as pressure measurement is around the room temperature and the molarity of solution is used instead of molality. As compared to other colligative properties, its magnitude is large even for very dilute solutions. The technique of osmotic pressure for determination of molar mass of solute is particularly useful for biomolecules as they are generally not stable at higher temperature and polymers have poor solubility.

Osmotic pressure of mixture of two solutions

Case I: Let two solutions of same substance having different osmotic pressures π_1 and π_2 are mixed. The osmotic pressure of the resultant solution can be calculated as

$$\pi_1 V_1 + \pi_2 V_2 = \pi_R (V_1 + V_2)$$

where V_1 and V_2 are the volumes of two solutions and π_R is the resultant osmotic pressure.

Case II: Let n_1 and n_2 are the number of moles of two different solutes present in V_1 and V_2 volumes, respectively.

The osmotic pressure of the mixture can be calculated as

$$\pi = \pi_1 + \pi_2 = \frac{n_1 i_1 RT}{(V_1 + V_2)} + \frac{n_2 i_2 RT}{(V_1 + V_2)}$$

$$\pi = \frac{(n_1 i_1 + n_2 i_2) RT}{(V_1 + V_2)}$$

Here i_1 and i_2 are Van't Hoff factor for the two solutes.

Isotonic, Hypertonic, and Hypotonic Solutions

When two solutions of different osmotic pressure are separated by semi-permeable membrane, the solvent molecules flow from the solutions of lower osmotic pressure towards the solution of higher osmotic pressure. This process continue till both the solutions attain the same osmotic pressure. At this stage, there is no further osmosis. Such solutions having same osmotic pressure are called *isotonic* solutions or *isomotic pressure*.

From the equation, $\pi = CRT$, it is clear that if two solutions have same concentrations, they must have same osmotic pressure at same temperature. Thus, solutions of equimolar concentrations at the same temperature have same osmotic pressure, i.e., are *isotonic*. If a solutions has more osmotic pressure than some other solution, it is called *hypertonic*. On the other hand a solution having less osmotic pressure than the other solution is called *hypotonic solution*. Thus, a hypertonic solution is more concentrated with respect to other solution and a hypotonic solution is less concentrated with respect to the other solution. For example, the osmotic pressure associated with the fluid inside the blood cell is equivalent to that of 0.9% (mass/volume) NaCl solutions (i.e., isotonic) called normal saline solution, and it is safe to inject intravenously. On the other hand if we place the cells in a

solution containing more than 0.9% NaCl, water will flow out of the cells and they would shrink (i.e., hypertonic solution). If the salt concentration is less than 0.9% (hypotonic solution), water will flow into the cells and they would swell.

Experimental method for determination of osmotic pressure

There are various methods employed experimentally to determine osmotic pressure, few of them are listed below:

- Pfeffer's method
- Morse and Frazer's method
- Berkeley and Hartley's method

From the above-listed methods, Berkeley and Hartley's method is widely used.

Biological Importance of Osmosis

The growth of plants and animals depends largely on the phenomenon of osmosis. Plant and animal bodies are composed of a very large number of microscopic units called *cells*. Cells contain a fluid and are composed of a living cytoplasmic membrane which behaves as semi-permeable membrane and is responsible for the phenomenon of osmosis in living organism.

When a cell comes in contact with water or some dilute solution, the osmotic pressure of which is less than that of cell fluid present into the cell, there becomes a tendency of water to enter into the cell through the cell wall. This causes rupturing of the cell, a process known as *hemolysis*. The pressure developed inside the cell due to the inflow of water into it is called *turgor*. On the other hand, if the cell comes in contact with a solution of higher osmotic pressure, the cell would shrink due to the water going out of the cell through the cell wall. This shrinking of the cell is called *plasmolysis* or *crenation*.

Following are some processes regulated by osmosis in plants and animals:

- Plants absorb water from the soil through their roots due to osmosis because the concentration of cell sap inside root hair cells is higher than that of the water present in the soil.
- Osmosis helps in the rapid growth of plants and in the germination of seeds.
- Bursting of red blood cells when placed in water is also due to osmosis.
- Different movements of plants such as opening and closing of flowers, etc., are controlled by osmosis.
- A 0.91% solution of pure NaCl is *isotonic* with human red blood cells (RBCs). Therefore, in this solution, RBCs neither swell nor undergo plasmolysis.
- A pure NaCl solution with concentration less than 0.91% is called *hypotonic solution*. On placing RBCs in this solution, they will swell and even burst.
- A pure NaCl solution with concentration more than 0.91% is called *hypertonic solution*. On placing RBCs in this solution, they shrink due to plasmolysis.
- People taking a lot of salt or salty food experience water retention in tissue cells and intercellular spaces because of osmosis. The resulting puffiness or swelling is called *edema*.

- The use of salt and sugar as preservatives in pickles and jams has its basis in preventing growth of fungi and bacteria by osmosis.

2.10.5 REVERSE OSMOSIS

The direction of osmosis can be reversed by applying higher pressure than the osmotic pressure to the solution side. As a result of this the solvent starts flowing from solution side towards the pure solvent through the semi-permeable membrane. Thus, *reverse osmosis* is the process of movement of solvent through semi-permeable membrane from the solution to the pure solvent by applying excess pressure on the solution side.

This phenomenon has got a great practical utility. Reverse osmosis is used in water purification and desalination of sea water. For this purpose a variety of polymers are available these days. The pressure required for the reverse osmosis is quite high. A workable porous membrane is a film of cellulose acetate placed over a suitable support. Cellulose acetate is permeable to water but impermeable to impurities and ions present in sea water.

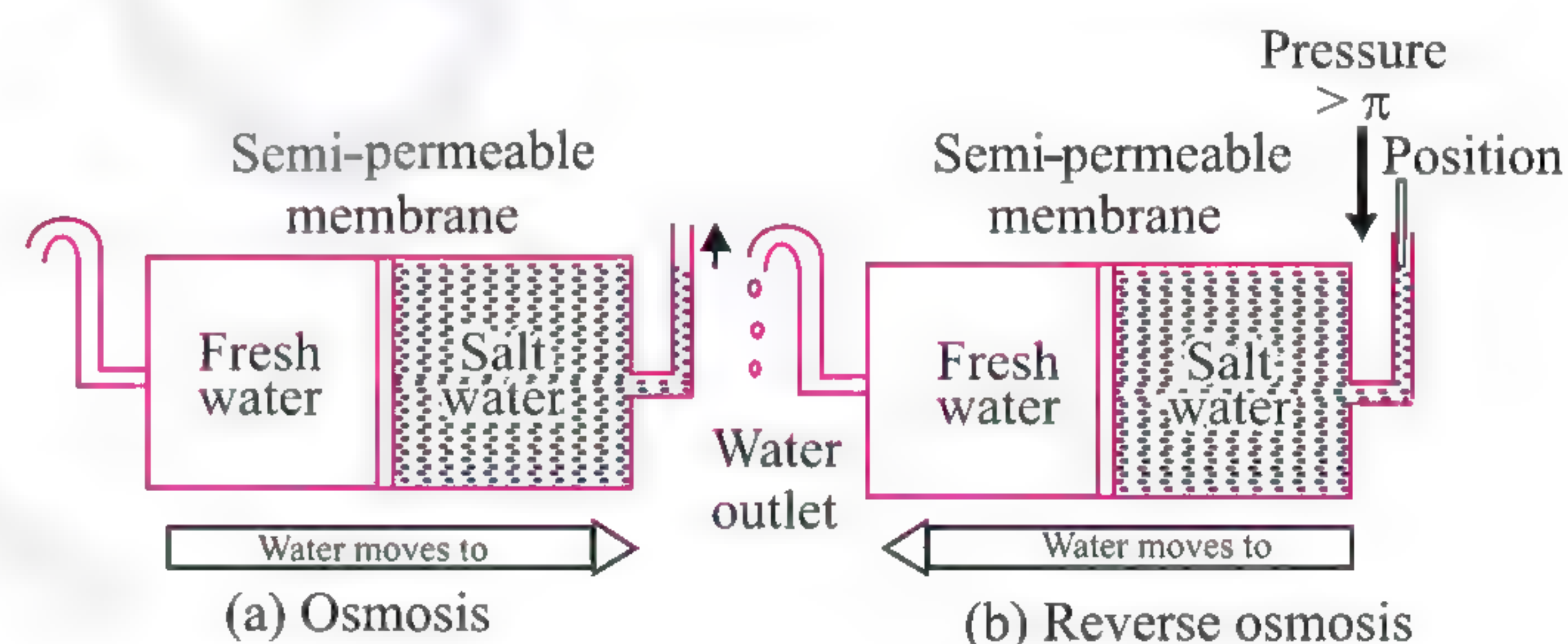


Fig. 2.22 A schematic set up for the reverse osmosis used for desalination of sea water

In Fig. 2.22(a), when there is no any external pressure applied to the salt water solution, fresh water flows towards salt water through semi-permeable membrane due to osmosis process. When a pressure greater than the osmotic pressure (π) is applied on the salt water [Fig. 2.22(b)], the pure water flows from the salt water side to pure water side through semi-permeable membrane. As a result water is squeezed out of sea water. Thus, pure water is obtained which does not contain any dissolved undesirable salt.

2.10.6 RELATIONSHIPS BETWEEN DIFFERENT COLLIGATIVE PROPERTIES

Osmotic Pressure (π) with Relative Lowering of Vapour Pressure

$$\text{Osmotic pressure } (\pi) = CRT = \frac{n_2}{V} RT \quad \dots(i)$$

Relative lowering of vapour pressure

$$\Rightarrow \frac{P^\circ - P_s}{P^\circ} = \chi_2 \approx \frac{n_2}{n_1}$$

$$\begin{aligned} \text{or } n_2 &= n_1 \times \left(\frac{P^\circ - P_s}{P^\circ} \right) \\ &= \frac{W_1}{M_{w1}} \left(\frac{P^\circ - P_s}{P^\circ} \right) \quad \dots(ii) \end{aligned}$$

Substituting Eq. (ii) in Eq. (i),

$$\pi = \frac{W_1 RT}{VMW_1} \left(\frac{P^\circ - P_s}{P^\circ} \right)$$

$$= \frac{dRT}{MW_1} \left[\frac{P^\circ - P_s}{P^\circ} \right] \quad \left[d(\text{density}) = \frac{W_1}{V} \right]$$

Osmotic Pressure (π) with Elevation in Boiling Point (ΔT_b)

$$\text{Elevation in boiling point } (\Delta T_b) = K_b m = \frac{K_b \times n_2 \times 1000}{W_1}$$

$$\text{or } n_2 = \frac{\Delta T_b \times W_1}{K_b \times 1000} \quad \dots(\text{iii})$$

Substituting Eq. (iii) in Eq. (i),

$$\pi = \frac{\Delta T_b \times W_1 \times RT}{V \times K_b \times 1000}$$

$$= \frac{\Delta T_b RT}{K_b \times 1000} \times \frac{W_1}{V} = \frac{\Delta T_b RT \times d}{K_b \times 1000} \quad \left[d = \frac{W_1}{V} \right]$$

Osmotic Pressure (π) with Depression in Freezing Point (ΔT_f)

$$\text{Depression in freezing point } (\Delta T_f) = K_f m = \frac{K_f \times n_2 \times 1000}{W_1}$$

$$\text{or } n_2 = \frac{\Delta T_f \times W_1}{K_f \times 1000} \quad \dots(\text{iv})$$

Substituting Eq. (iv) in Eq. (i),

$$\pi = \frac{\Delta T_f \times W_1 \times RT}{K_f \times 1000 \times V}$$

$$= \frac{\Delta T_f \times dRT}{K_f \times 1000} \quad \left[d = \frac{W_1}{V} \right]$$

Elevation in Boiling Point with Relative Lowering of Vapour Pressure

$$\text{Elevation in boiling point } (\Delta T_b) = K_b m = \frac{K_b \times n_2 \times 1000}{W_1} \quad \dots(\text{v})$$

Relative lowering of vapour pressure

$$\frac{P^\circ - P_s}{P^\circ} = \chi_2 \approx \frac{n_2}{n_1} = \frac{n_2}{n_1} \times MW_1 \quad \left[n_1 = \frac{W_1}{MW_1} \right]$$

$$\text{or } n_2 = \left(\frac{P^\circ - P_s}{P^\circ} \right) \times \frac{W_1}{MW_1} \quad \dots(\text{vi})$$

Substituting Eq. (vi) in Eq. (v),

$$\therefore \Delta T_b = \frac{1000 \times K_b}{MW_1} \left(\frac{P^\circ - P_s}{P^\circ} \right)$$

Depression in Freezing Point with Lowering of Vapour Pressure

$$\text{Depression in freezing point } (\Delta T_f) = K_f m = \frac{K_f \times n_2 \times 1000}{W_1} \quad \dots(\text{vii})$$

Lowering in vapour pressure

$$\frac{P^\circ - P_s}{P^\circ} = \chi_2 \approx \frac{n_2}{n_1} = \frac{n_2}{n_1} \times MW_1 \quad \left[n_1 = \frac{W_1}{MW_1} \right]$$

$$\therefore n_2 = \left(\frac{P^\circ - P_s}{P^\circ} \right) \times \frac{W_1}{MW_1} \quad \dots(\text{viii})$$

Substituting Eq. (viii) in Eq. (vii),

$$\therefore \Delta T_f = \frac{1000 \times K_f}{MW_1} \left(\frac{P^\circ - P_s}{P^\circ} \right)$$

ILLUSTRATION 2.141

Define osmotic pressure.

Sol. Osmotic pressure is the extra pressure that is to be applied on the solution side when the solution and solvent are separated by a semi-permeable membrane to stop osmosis.

ILLUSTRATION 2.142

What is reverse osmosis?

Sol. When the hydrostatic pressure applied on the solution side is more than the osmotic pressure of solution, then solvent molecules from solution side enter in to the solvent side through semi-permeable membrane. This process is called reverse osmosis.

ILLUSTRATION 2.143

Briefly explain the underlying principle of the purification of water by reverse osmosis.

Sol. When pressure greater than osmotic pressure is applied on the salt water side of a semi-permeable membrane, water molecules flow through the membrane towards pure water side.

ILLUSTRATION 2.144

State how does osmotic pressure vary with temperature?

Sol. Osmotic pressure increases with increase in temperature.

ILLUSTRATION 2.145

What are isotonic solutions?

Sol. Two solutions which have the same osmotic pressure are called isotonic solutions.

ILLUSTRATION 2.146

Outer hard shells of two eggs are removed. One of the eggs is placed in pure water and the other is placed in saturated solution of sodium chloride. What will be observed and why?

Sol. The egg placed in water will swell due to the osmosis of pure water into the egg. On the other hand, the egg placed in the saturated solution of NaCl will shrink due to the osmosis of water out of the egg. This is because osmosis always occurs from higher concentration of solvent to lower concentration of solvent.

ILLUSTRATION 2.147

When dehydrated fruits and vegetables are placed in water, they slowly swell and return to original form. Why? Would a temperature increase accelerate the process? Explain.

Sol. The cell walls of fruits and vegetables are semi-permeable. The liquid inside the cells in the dried fruits and vegetables is more concentrated. When these dried fruits and vegetables are placed in water, water enters the fruits and vegetables due to osmosis and they swell and return to their original form. Since the increase in temperature increases the osmotic pressure ($\pi \propto T$), the process gets accelerated.

ILLUSTRATION 2.148

Why is great care taken in intravenous injections to have comparable concentration of solutions to be injected to that of blood plasma?

Sol. During intravenous injections, the concentrations of the solution to be injected should be comparable to blood plasma. If the solution is less concentrated, its osmotic pressure will be low. The water will try to move into the red blood cells through the cell walls. As a result, cells will swell and burst. On the other hand, if the solution is more concentrated, the water in the cells will try to move outside the cell to the more concentrated solution by osmosis. This causes cells to shrink and consequently cease to function.

ILLUSTRATION 2.149

Which colligative property is preferred for the molar mass determination of macromolecules (i.e., proteins and polymers)?

Sol.

- a. The molecular weight of macromolecules (e.g., proteins and polymers) is very high, hence the measured values $\left(\text{e.g., } \frac{\Delta P}{P^\circ}, \Delta T_f, \Delta T_b \right)$ will be very less and thus cannot be determined accurately.

Although the osmotic pressure will also be less but it can be measured, since it is not the difference in pressure as in the cases of other colligative properties.

- b. The osmotic pressure is measured at room temperature. So the properties of macromolecules do not change, whereas all other methods require heating which changes the properties of macromolecules, e.g., the proteins may coagulate and polymers may decompose at higher temperature.

ILLUSTRATION 2.150

Addition of HgI_2 to the aqueous solution of KI shows an increase in the osmotic pressure, why?

Sol. HgI_2 forms a complex with KI, and therefore, the number of particles in solution increases.



Therefore, the osmotic pressure increases.

ILLUSTRATION 2.151

What will happen if pressure greater than the osmotic pressure is applied on the solution separated by a semi-permeable membrane from the solvent?

Sol. It will result into reverse osmosis, i.e., there will be net flow of the solvent from the solution to the solvent.

ILLUSTRATION 2.152

What is osmotic pressure and how is it related with the molecular mass of a non-volatile substance? What advantage the osmotic pressure method has over the elevation of boiling point method for determining molecular masses?

Sol. For definition of osmotic pressure, refer to Section 2.10.4.

$$\pi V = nRT$$

$$\pi = \frac{n}{V} RT = \frac{W_B \times R \times T}{M_{wB} \times V}$$

$$M_{wB} = \frac{W_B \times R \times T}{\pi \times V},$$

where M_{wB} is the molar mass of the solute.

The advantage of the osmotic pressure method is that it is measured at room temperature. It is convenient to measure at room temperature than at boiling point. The value of osmotic pressure is quite appreciable even for very dilute solutions of polymers as compared to that of elevation boiling point.

ILLUSTRATION 2.153

Why a person suffering from high blood pressure is advised to take minimum quantity of common salt?

Sol. The osmotic pressure is directly proportional to the concentration of solutes. Our body fluid contains a number of solutes. On taking large amount of common salt, Na^+ and Cl^- ions enter into the body fluid thereby raising the concentration of the solutes. As a results, osmotic pressure is increased which may rupture the blood cells.

ILLUSTRATION 2.154

Blood freezes at 272.44 K and a solution of 3.0 g of urea in 250 g of water freezes at 272.63 K. Calculate the osmotic pressure of blood at 300 K. (Assume density of blood at 300 K to be 1 g cc^{-1})

Sol. In this question first calculate K_f of water from urea solution.

$$\Delta T_f = K_f \left(\frac{W_B}{M_{wB}} \times 1000 \right)$$

$$\Rightarrow K_f = \frac{\Delta T_f}{\left(\frac{W_B}{M_{wB}} \times 1000 \right)}$$

$$\Rightarrow K_f = \frac{0.37}{\left(\frac{3}{250} \times 1000 \right)} = 1.85 \quad [\Delta T_f = 273 - 272.63 = 0.37 \text{ K}]$$

Now determine the molality of blood by using

$$\Delta T_f = K_f m$$

$$\text{Now } \Delta T_f = 273 - 272.44 = 0.56^\circ\text{C}$$

$$m = \frac{\Delta T_f}{K_f} = \frac{0.56}{1.85} = 0.303$$

Note: Colligative properties are defined for dilute solution. Assume molarity = molality.

$$\Rightarrow \text{Molarity} = \text{molality} = 0.303$$

$$\text{Now using } \pi = CRT$$

$$\Rightarrow \pi = 0.303 \times 0.082 \times 300 = 7.46 \text{ atm}$$

ILLUSTRATION 2.155

x g of non-electrolytic compound (molar mass = 200) is dissolved in 1.0 L of 0.05 M NaCl solution. The osmotic pressure of this solution is found to be 4.92 atm at 27°C . Calculate the value of x . Assume complete dissociation of NaCl and ideal behaviour of this solution.

Sol.

$$\text{a. For NaCl: } \pi = iCRT = 2 \times 0.05 \times 0.0821 \times 300 = 2.463$$

b. For unknown compound:

$$\pi = CRT = \frac{x}{200} \times 0.0821 \times 300 = 0.1231x \text{ atm}$$

$$\text{Total osmotic pressure } \pi = \pi_1 + \pi_2$$

$$4.92 = 2.463 + 0.1231x$$

$$x = 19.959 \text{ g}$$

ILLUSTRATION 2.156

The osmotic pressure of a solution is 1.3 atm. The density of solution is 1.3 g cm^{-3} . Calculate the osmotic pressure rise. ($1 \text{ atm} = 76 \text{ cm Hg}$, $d_{\text{Hg}} = 13.6 \text{ g cm}^{-3}$)

Sol. $\pi = h d g$

$$1.3 \times 76 \times 13.6 \times g = h \times 1.1 \times g$$

$$h = \frac{1.3 \times 76 \times 13.6}{1.3} \text{ cm} = 1033.6 \text{ cm}$$

ILLUSTRATION 2.157

Two solutions of glucose have osmotic pressure 1.5 and 2.5 atm, respectively. 1 L of first solution is mixed with 2 L of second solution. The osmotic pressure of the resultant solution will be

a. 2.62 atm b. 6.12 atm c. 3.26 atm d. 2.16 atm

Sol. d. $\pi_1 V_1 + \pi_2 V_2 = \pi_R (V_1 + V_2)$

$$1.5 \times 1 + 2.5 \times 2 = \pi_R \times 3$$

$$\pi_R = \frac{6.5}{3} = 2.16 \text{ atm}$$

ILLUSTRATION 2.158

18 g glucose and 6 g urea are dissolved in 1 L aqueous solution at 27°C . The osmotic pressure of the solution will be

a. 8.826 atm b. 4.926 atm
c. 2.92 atm d. 4.42 atm

Sol. b. $\pi V = (n_1 + n_2) RT$

$$\pi V = \left(\frac{W_1}{Mw_1} + \frac{W_2}{Mw_2} \right) RT$$

$$\pi \times 1 = \left(\frac{18}{180} + \frac{6}{60} \right) \times 0.0821 \times 300$$

$$\pi = 4.926 \text{ atm}$$

ILLUSTRATION 2.159

The osmotic pressure of decimolar solution of urea at 27°C is

a. 2.49 bar b. 5 bar c. 3.4 bar d. 1.25 bar

Sol. a. $\pi = CRT$

$$= 0.1 \times 0.083 \times 300$$

$$= 2.49 \text{ bar}$$

ILLUSTRATION 2.160

The osmotic pressure of a solution at 0°C is 4 atm. What will be its osmotic pressure at 546 K under similar conditions?

a. 4 atm b. 9 atm c. 8 atm d. 6 atm

Sol. c. $\frac{\pi_1}{\pi_2} = \frac{CRT_1}{CRT_2}$

$$\frac{\pi_1}{\pi_2} = \frac{T_1}{T_2}$$

$$\frac{4}{\pi_2} = \frac{273}{546}$$

$$\pi_2 = 8 \text{ atm}$$

ILLUSTRATION 2.161

3% solution of glucose is isotonic with 1% solution of non-volatile non-electrolyte solute. The molecular mass of the solute would be

a. 180 b. 160 c. 120 d. 60

Sol. d. $\pi_{\text{glucose}} = \pi_{\text{solute}}$

$$C_{\text{glucose}} = C_{\text{solute}}$$

$$\left(\frac{W_B \times 1000}{Mw_B \times V} \right)_{\text{glucose}} = \left(\frac{W_B \times 1000}{Mw_B \times V} \right)_{\text{solute}}$$

$$\left(\frac{3 \times 1000}{180 \times 100} \right)_{\text{glucose}} = \left(\frac{1 \times 1000}{Mw_B \times 100} \right)_{\text{solute}}$$

$$Mw_B(\text{solute}) = 60$$

ILLUSTRATION 2.162

300 cm³ of an aqueous solution contains 1.26 g a polymer. The osmotic pressure of such solution at 300 K is found to be 1.26×10^{-3} bar. Calculate the molar mass of the polymer.

Sol. $\pi V = \frac{W_B}{M_{w_B}} RT$

$$M_{w_B} = \frac{W_B}{V} \times \frac{RT}{\pi}$$

$$= \frac{1.26}{0.3} \times \frac{0.083 \times 300}{1.26 \times 10^{-3}}$$

$$= 83000 \text{ g mol}^{-1}$$

ILLUSTRATION 2.163

The solution containing 10 g of an organic compound per litre showed an osmotic pressure of 1.18 atm at 0°C. Calculate the molecular mass of the compound ($R = 0.0821$ litre atm per degree per mol)

Sol. Applying the equation

$$M_w = \frac{W}{PV} \cdot RT$$

Given, $W = 10$ g, $P = 1.18$ atm, $V = 1$ L, $R = 0.0821$ and $T = 273$ K.

$$M_w = \frac{10}{1.18 \times 1} \times 0.0821 \times 273 = 189.94$$

ILLUSTRATION 2.164

Calculate the osmotic pressure of 5% solution of cane sugar (sucrose) at 300 K.

Sol. $M_w =$ Molecular mass of sucrose ($C_{12}H_{22}O_{11}$) = 342

$W = 5$ g, $V = 300 \text{ mL} = 0.3$ L

$R = 0.082$, $T = 300$ K

Applying the equation $\pi V = \frac{W}{M_w} RT$

$$\pi = \frac{5}{342} \times \frac{1}{0.3} \times 0.082 \times 300$$

$$= 1.198 \text{ atm}$$

ILLUSTRATION 2.165

A solution is prepared by dissolving 1.08 g of human serum albumin, a protein obtained from blood plasma, in 50 cm³ of aqueous solution. The solution has an osmotic pressure of 5.85 mm Hg at 298 K.

- What is the molar mass of albumin?
- What is the height of water column placed in solution?
 $d_{(H_2O)} = 1 \text{ g cm}^{-3}$

Sol.

- The molar mass of albumin can be calculated using the following relation

$$M_{w_B} = \frac{W_B \times RT}{\pi V} \quad \dots(i)$$

Given, $W_B = 1.08$ g; $R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$

$T = 298$ K, $\pi = \frac{5.85}{760}$ atm; $V = \frac{50}{1000} = 0.05$ L

Substituting these values in Eq. (i), we get

$$M_{w_B} = \frac{1.08 \times 0.0821 \times 298}{(5.85/760) \times 0.05} = 68655 \text{ g mol}^{-1}$$

- $\pi = h d g$

$$\frac{5.85}{760} \times 101325 = h \times 1 \times 10^{-3} \times 9.8 \quad [1 \text{ atm} = 101325 \text{ Pa}]$$

$$\therefore h = 7.958 \times 10^{-2} \text{ m} = 7.958 \text{ cm}$$

ILLUSTRATION 2.166

A 5% solution of cane sugar is isotonic with 0.877% solution of urea. Calculate the molecular mass of urea if the molecular mass of cane sugar is 342.

Sol. Let the molecular mass of urea be M_{w_2} .

$$\text{Molar concentration of sugar} = \frac{W_1}{M_{w_1} \times V_1} = \frac{5}{342 \times 0.1}$$

$$\text{Molar concentration of urea} = \frac{W_2}{M_{w_2} \times V_2} = \frac{0.877}{M_{w_2} \times 0.1}$$

For isotonic solution,

$$\frac{W_1}{M_{w_1} V_1} = \frac{W_2}{M_{w_2} V_2}$$

$$\frac{5}{342 \times 0.1} = \frac{0.877}{M_{w_2} \times 0.1}$$

$$M_{w_2} = \frac{0.877 \times 342}{5}$$

$$= 59.987$$

ILLUSTRATION 2.167

200 cm³ of an aqueous solution of a protein contains 1.26 g of the protein. The osmotic pressure of such a solution at 300 K is found to be 2.57×10^{-3} bar. Calculate the molar mass of the protein.

Sol. The given values are

$$\pi = 2.57 \times 10^{-3} \text{ bar}$$

$$V = 200 \text{ cm}^3 = 0.2 \text{ L}$$

$$T = 300 \text{ K}$$

$$R = 0.083 \text{ L bar mol}^{-1} \text{ K}^{-1}$$

Using the formula,

$$M_{w_{\text{solute}}} = \frac{W_{\text{solute}} \times R \times T}{\pi \times V}$$

$$= \frac{1.26 \text{ g} \times 0.083 \text{ L bar mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{2.57 \times 10^{-3} \text{ bar} \times 0.2 \text{ L}}$$

$$= 61022 \text{ g mol}^{-1}$$

Thus, the molecular weight of solute is 61022 g mol^{-1} .

ILLUSTRATION 2.168

At 300 K, 36 g of glucose present per litre in its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of the solution is 1.52 bar at the same temperature, what would be its concentration?

Sol. The given values are

$$T = 300 \text{ K}$$

$$W_{\text{solute}} = 36 \text{ g}$$

$$\pi_1 = 4.98 \text{ bar}$$

$$\pi_2 = 1.52 \text{ bar}$$

$$V_{\text{solution}} = 1 \text{ L}$$

According to Van't Hoff equation,

$$\pi = CRT$$

$$C_1 = \frac{36}{180} \text{ M}, \quad C_2 = ?$$

$$\therefore 4.98 \text{ bar} = \frac{36}{180} RT \quad \dots(i)$$

$$1.52 \text{ bar} = C_2 RT \quad \dots(ii),$$

Dividing Eq. (ii) by Eq. (i),

$$\frac{C_2}{36} \times 180 = \frac{1.52}{4.98}$$

$$\therefore C_2 = \frac{1.52}{4.98} \times \frac{36}{180} = 0.061 \text{ M}$$

Thus, the concentration of second solution is 0.061 M.

ILLUSTRATION 2.169

The osmotic pressure of blood is 8.21 atm at 310 K. How much glucose should be used per L for an intravenous injection that is isotopic with blood?

Sol. The given values are

$$\pi_{(\text{blood})} = 8.21 \text{ atm}; V = 1 \text{ L}; T = 310 \text{ K}$$

$$\pi_{(\text{glucose})} = 8.21 \text{ atm} \quad (\text{blood and glucose are isotonic})$$

$$\text{Now, } \pi V = nRT$$

$$\text{or } n = \frac{\pi V}{RT}$$

$$\therefore n = \frac{8.21 \times 1.0}{0.0821 \times 300} = \frac{10}{31}$$

$$\begin{aligned} \therefore \text{Weight of glucose} &= n \times \text{Molecular weight} \\ &= \frac{10}{31} \times 180 = 58.06 \text{ g} \end{aligned}$$

ILLUSTRATION 2.170

A solution was prepared by dissolving 6.0 g an organic compound in 100 g of water. Calculate the osmotic pressure of this solution at 298 K, when the boiling point of the Solution is 100.2°C . (K_b for water = 0.52 K m^{-1} , $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$)

Sol. The given values are

$$W_{\text{solute}} = 6.0 \text{ g}; W_{\text{solvent}} = 100 \text{ g}, K_b = 0.52 \text{ K m}^{-1}$$

$$\Delta T_b = 100.2 - 100 = 0.2$$

Now using the formula

$$\begin{aligned} M_{w_{\text{solute}}} &= \frac{K_b \times W_{\text{solute}} \times 1000}{\Delta T_b \times W_{\text{solvent}}} \\ &= \frac{0.52 \times 6.0 \times 1000}{0.2 \times 100} \\ &= 156 \text{ g mol}^{-1} \end{aligned}$$

$$\text{Now, } \pi = \frac{nRT}{V}; \quad n = \frac{W_{\text{solute}}}{M_{w_{\text{solute}}}}$$

$$\therefore n = \frac{6.0}{156}$$

$$\therefore \pi = \frac{6.0 \times 0.082 \times 298}{156 \times 0.1}$$

$$= 9.398 \text{ atm}$$

Thus, the osmotic pressure of the solution is 9.398 atm.

ILLUSTRATION 2.171

A solution obtained by mixing 100 mL of 20% solution of urea (molar mass = 60) and 100 mL of 1.6% solution of cane sugar (molar mass = 342) at 300 K. ($R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}$). Calculate

- Osmotic pressure of urea solution
- Osmotic pressure of cane sugar solution
- Total osmotic pressure of solution

Sol. The given values are

$$W_{\text{urea}} = 2.0 \text{ g}; V = 200 \text{ mL}, T = 293 \text{ K}$$

$$W_{\text{cane sugar}} = 1.2 \text{ g}; M_{w_{\text{urea}}} = 60, M_{w_{\text{cane sugar}}} = 342$$

$$R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}$$

Now using Van't Hoff equation,

$$\pi = CRT \text{ or } \frac{W_2 RT}{M_{w_2} V}$$

- Osmotic pressure of urea

$$\pi = \frac{2.0 \times 0.083 \times 300}{60 \times 0.2} = 4.15 \text{ bar}$$

- Osmotic pressure of cane sugar

$$\pi = \frac{1.2 \times 0.083 \times 300}{342 \times 0.2} = 0.43 \text{ bar}$$

- The total osmotic pressure of solution will be the sum of the osmotic pressure produced by urea and cane sugar, respectively.

$$\begin{aligned} \therefore \pi_{\text{total}} &= \pi_{\text{urea}} + \pi_{\text{cane sugar}} \\ &= 4.15 + 0.43 = 4.58 \text{ bar} \end{aligned}$$

ILLUSTRATION 2.172

The osmotic pressure of a solution containing 5 g of substance (molar mass = 100) in 308 mL of solution was found to be 4.0 atm at 300 K. Calculate the value of solution constant (R).

Sol. The given values are

$$W_B = 5 \text{ g}; \quad M_{w_B} = 100 \text{ g mol}^{-1}$$

$$\pi = 4.0 \text{ atm}; \quad T = 300 \text{ K}; \quad V = 308 \text{ mL}$$

Using formula,

$$R = \frac{\pi V}{nT} = \frac{4.0 \times \frac{308}{1000}}{\frac{5}{100} \times 300} = 0.0821 \text{ L-atm mol}^{-1} \text{ degree}^{-1}$$

ILLUSTRATION 2.173

The osmotic pressure of a solution was found to be 8 atm when 8 mol of a non-volatile solute was dissolved in V L of solution at 300 K. Calculate the volume of solution ($R = 0.0821 \text{ L-atm K}^{-1} \text{ mol}^{-1}$)

Sol. The given values are

$$\pi = 8 \text{ atm}; \quad T = 300 \text{ K}; \quad n_B = 8$$

$$R = 0.0821 \text{ L-atm mol}^{-1}$$

Now, using formula

$$V = \frac{nRT}{\pi} = \frac{8 \times 0.0821 \times 300}{8} = 246.3 \text{ L}$$

ILLUSTRATION 2.174

A solution of an organic compound is prepared by dissolving 30 g in 100 g water. Calculate the molecular mass of compound and the osmotic pressure of solution at 300 K, when the elevation in boiling point is 0.52 and K_b for water is 0.52 K m^{-1} .

Sol. The given values are

$$W_B = 30 \text{ g}; \quad W_A = 100 \text{ g}; \quad T = 300 \text{ K}$$

$$\Delta T_b = 0.52; \quad K_b = 0.52 \text{ K m}^{-1}$$

Now, using formula

$$M_{w_B} = \frac{K_f \times 1000 \times W_B}{W_A \times \Delta T_b} = \frac{0.52 \times 1000 \times 30}{100 \times 0.52} = 300 \text{ g}$$

For osmotic pressure,

$$\pi = \frac{nRT}{V} = \frac{W_B}{M_{w_B}} \times \frac{R \times T}{V} = \frac{30}{300} \times \frac{0.082 \times 300}{100/1000} = 2.46 \text{ atm}$$

ILLUSTRATION 2.175

What will be the osmotic pressure of 0.1 M monobasic acid its pH is 2 at 25°C?

Sol. $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$

$$[\text{H}^+] = C\alpha = 10^{-2} \text{ M}$$

$$\therefore \alpha = \frac{10^{-2}}{0.1} = 10^{-1} = 0.1$$

$$\therefore \text{Total particles in solution} = 1 + \alpha = 1 + 0.1 = 1.1$$

$$\text{Now, } \pi = CRT(1 + \alpha)$$

$$= 0.1 \times 0.0821 \times 298 \times 1.1$$

$$= 2.69 \text{ atm}$$

ILLUSTRATION 2.176

100 mL of 1.0 g sample of a drug having compound $\text{C}_{21}\text{H}_{23}\text{O}_5\text{N}$ as drug is coated with sugar lactose (mol. wt. 342) exerts the osmotic pressure of 0.70 atm at 27°C. What is the drug percentage in sample?

Sol. Let a , b g are the amount of drug ($M_w = 369$) and sugar ($M_w = 342$), respectively

$$a + b = 1.0 \dots (i)$$

$$\therefore \pi V = (n_1 + n_2) RT$$

$$0.70 \times \frac{100}{1000} = \left[\frac{a}{369} + \frac{b}{342} \right] \times 0.0821 \times 300$$

$$342a + 369b = 358.66 \dots (ii)$$

By Eqs. (i) and (ii)

$$a = 0.617 \text{ g}$$

$$b = 0.383 \text{ g}$$

$$\therefore \% \text{ of drug} = \frac{0.617}{1} \times 100 = 61.7\%$$

ILLUSTRATION 2.177

At 10°C, the osmotic pressure of urea solution is 500 mm. The solution is diluted and the temperature is raised to 25°C, when the osmotic pressure is found to be 105.3 mm. Determine the extent of dilution.

Sol. For initial solution, $\pi = \frac{500}{760} \text{ atm}$, $T = 283 \text{ K}$

$$\text{Using } \pi V = nRT$$

$$\Rightarrow \frac{500}{760} \times V_1 = n \times R \times 283 \dots (i)$$

After dilution, let volume becomes V_2 and temperature is raised to 25°C, i.e., 298 K.

$$\pi = \frac{105.3}{760} \text{ atm}$$

$$\frac{105.3}{760} \times V_2 = n \times R \times 298 \dots (ii)$$

\therefore By Eqs. (i) and (ii), we get

$$\frac{V_1}{V_2} = \frac{283}{298} \times \frac{105.3}{500}$$

$$\frac{V_1}{V_2} = \frac{1}{5}$$

$$\Rightarrow V_2 = 5V_1$$

i.e., the solution was diluted to 5 times.

CONCEPT APPLICATION EXERCISE 2.2

1. The vapour pressure of ethyl alcohol at 25°C is 59.2 torr. The vapour pressure of a solution of non-volatile solute urea NH_2CONH_2 in ethyl alcohol is 51.3 torr. What is the molality of solution?
2. 30 mL of methyl alcohol (density = 0.8 g cm⁻³) is mixed with 70 mL of water (density = 1.0 g cm⁻³) at 25°C to give a solution of density 0.94 g cm⁻³. Find the mole fraction, molarity, and molality.
3. In winter, the normal temperature in a Himalayan's valley was found to be -10°C. Is a 30% by mass of aqueous solution of ethylene glycol (molar mass = 62) suitable for car radiator? (K_f for water = 1.86 K m⁻¹)
4. The vapour pressure of a very dilute aqueous solution and pure water is 17 and 17.39 mm at 20°C, respectively. Calculate the osmotic pressure at 20°C and density of water vapour at 20°C.

ANSWERS

1. $m = 3.33$
2. $\chi_B = 0.16$; $\chi_A = 0.84$; Molarity = 7.5; molality = 10.58
3. -12.86 4. $\pi = 30.66$ atm; $d_{\text{H}_2\text{O}} = 1.673 \times 10^{-5}$ g mol⁻¹

2.11 ABNORMAL MOLAR MASSES: ELECTROLYTIC SOLUTIONS

Experiments on colligative properties of a solution reveals trustworthy results only if the following conditions are satisfied:

a. *The solution must not be too concentrated*

If the solution is concentrated, the particle begins to interact with each other as much as with the solvent. This obviously means that the vapour pressure starts to depend on the nature of the solute, and not just on the number of solute particles. Hence, to get the accurate values of molar mass the solution should be very dilute.

b. *The solute must not undergo dissociation or association in the solution*

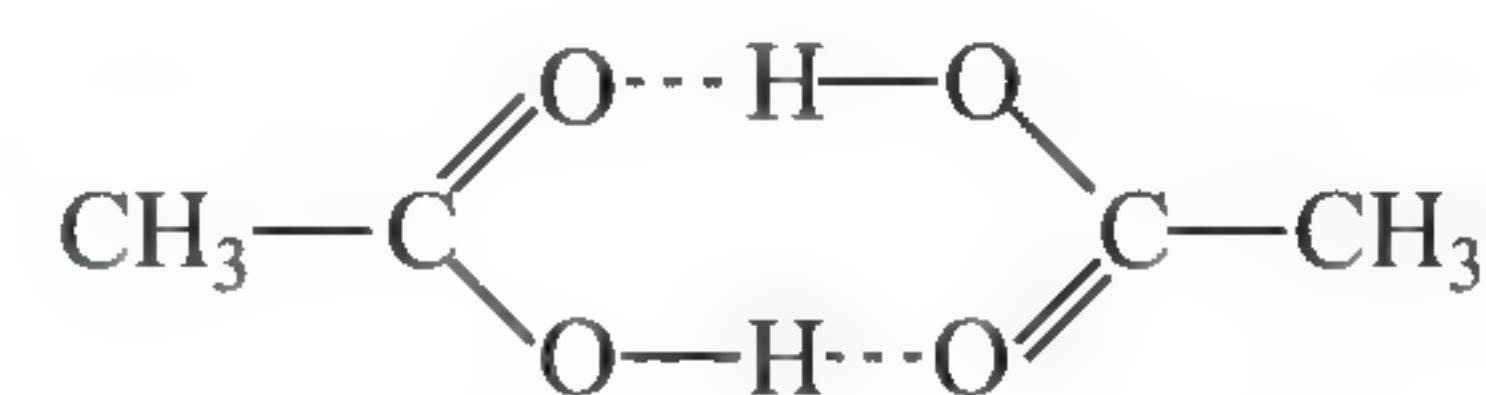
As we know that colligative properties depend only upon the number of particles present in the solution irrespective to their nature, if the solute particle undergoes dissociation or association, the number of particles in solution changes and as a result of this the colligative properties also change. This result of discrepancy in the determination of molar mass of solute is called *abnormal molar mass*.

Let us discuss abnormal molar masses due to association or dissociation of solute particles. These two changes are being discussed below:

a. *Association of solute particles*

In a solvent of low dielectric constant or being non-polar, the solute molecules undergo association, i.e., two, three, or more molecules exist in combination with each other to form

bigger molecules. For example, molecules of ethanoic acid (acetic acid) dimerize in benzene due to hydrogen bonding as shown below.



Ethanoic acid dimer

Therefore, the total number of molecules in solution becomes less than the number of molecules of the substance added and therefore, colligative properties will be lower.

Since the colligative properties are inversely proportional to the molar mass of the solute, the molar masses will be greater than the theoretical values. Then, ΔT_b or ΔT_f for ethanoic acid will be half of the normal value. The molar mass calculated on the basis of this ΔT_b or ΔT_f will, therefore, be twice the expected value.

b. *Dissociation of solute molecules*

Let us suppose a solute gets dissociated or ionize in a solvent to give two or more particles. For example, a solute AB dissociates to give cation and anion as:



Consequently, the total number of particles becomes twice in the solution and hence the colligative properties of such particles will be large and as the result of this the molar mass will be half the theoretical value.

For example, if we dissolve one mole of NaCl (58.5 g) in water, we expect one mole of each of K^{\oplus} and Cl^{\ominus} ions to be released in the solution. If this happens, there would be two moles of particles in the solution. Consequently, the colligative properties would also be about double than the expected. If we ignore interionic attraction, 1 mol of NaCl in 1 kg of water would be expected to increase the boiling point by 2×0.52 K ($K_b = 0.52$ K m⁻¹) = 1.04 K. Obviously the molar mass of the salt must be about half of its normal value, i.e., 37.5 g.

2.12 VAN'T HOFF FACTOR

When molecules in a solution undergo association and dissociation, the colligative property for such solution is different from the ideal solution. This change in the property was explained by Van't Hoff. In 1880, Van't Hoff introduced a factor i , known as the *Van't Hoff factor*, to account for the extent of dissociation or association.

This factor i is defined as

$$i = \frac{\text{Normal (calculated) molecular mass}}{\text{Abnormal (observed) molecular mass}}$$

$$= \frac{Mw_{\text{(calculated)}}}{Mw_{\text{(observed)}}} \text{ or } \frac{Mw_c}{Mw_o}$$

or

$$i = \frac{\text{Total number of moles of particles after dissociation/association}}{\text{Number of moles of particles before dissociation/association}}$$

In case of association, observed molar mass being more than the normal, the factor i has value less than 1. But in case of dissociation, the Van't Hoff factor is more than 1 because the observed molar mass has a lesser value.

In case of solute which does not undergo any association or dissociation in a solvent, the Van't Hoff factor i will be equal to 1 because the observed and normal molar masses will be same.

Since the molar masses are inversely proportional to the colligative property, the Van't Hoff factor may also be expressed as:

$$\begin{aligned}
 i &= \frac{\text{Observed value of colligative property}}{\text{Calculated colligative property}} \\
 &= \frac{P_{\text{obs}}}{P_{\text{calculated}}} = \frac{(\Delta P)_{\text{obs}}}{(\Delta P)_{\text{calculated}}} \\
 &= \frac{(\Delta T_b)_{\text{obs}}}{(\Delta T_b)_{\text{calculated}}} = \frac{(\Delta T_f)_{\text{obs}}}{(\Delta T_f)_{\text{calculated}}} \\
 &= \frac{\text{Actual number of particles in solution}}{\text{Number of particles taken}}
 \end{aligned}$$

Here, the calculated colligative properties are obtained by assuming that the non-volatile solute is neither associated or dissociated.

For example, the value of i for aqueous KCl solution is close to 2, while the value for ethanoic acid in benzene is nearly 0.5.

Table 2.5 depicts values of the factor i for several strong electrolytes. For KCl, NaCl, and MgSO_4 , Van't Hoff factor (i) approaches the value 2 as the solution becomes very dilute. As expected, the value of i gets close to 3 for K_2SO_4 . Table 2.6 illustrates the Van't Hoff factor (i) for different solutes.

Table 2.5 Values of Van't Hoff factor (i) at various concentrations for NaCl, KCl, MgSO_4 , and K_2SO_4

Salt	Values of i			i for complete dissociation
	0.1 m	0.01 m	0.001 m	
NaCl	1.87	1.94	1.97	2.00
KCl	1.85	1.94	1.98	2.00
MgSO_4	1.21	1.53	1.82	2.00
K_2SO_4	2.32	2.70	2.84	3.00

Table 2.6 Van't Hoff factor (i) for different solutes

S. No.	Solute type	Example	Ionization or association	Number of particles in the solution from 1 mol solute	Van't Hoff factor, i	Abnormal molecular mass
1.	Non-electrolyte	Urea, sucrose, glucose	—	1	1	$M_{w_{\text{normal}}}$
2.	Binary electrolyte AB type	NaCl, KCl CH_3COOH	$AB \rightleftharpoons A^{\oplus} + B^{\ominus}$ $1-\alpha \quad \alpha \quad \alpha$	2	$1 + \alpha$	$\frac{M_{w_{\text{normal}}}}{1 + \alpha}$
3.	Ternary electrolyte (AB_2 type or A_2B type)	$\text{CaCl}_2, \text{BaCl}_2$ $\text{H}_2\text{SO}_4, \text{K}_2[\text{PtCl}_6]$	$AB_2 \rightleftharpoons A^{2+} + 2B^{\ominus}$ $1-\alpha \quad \alpha \quad 2\alpha$ $A_2B \rightleftharpoons 2A^{\oplus} + B^{2-}$ $1-\alpha \quad 2\alpha \quad \alpha$	3 3	$1 + 2\alpha$ $1 + 2\alpha$	$\frac{M_{w_{\text{normal}}}}{1 + 2\alpha}$ $\frac{M_{w_{\text{normal}}}}{1 + 2\alpha}$
4.	Quaternary electrolyte (AB_3 or A_3B type)	$\text{AlCl}_3, \text{K}_3[\text{Fe}(\text{CN})_3]$ $\text{FeCl}_3, \text{K}_3\text{PO}_4$	$AB_3 \rightleftharpoons A^{3+} + 3B^{\ominus}$ $1-\alpha \quad \alpha \quad 3\alpha$ $A_3B \rightleftharpoons 3A^{\oplus} + B^{3-}$ $1-\alpha \quad 3\alpha \quad \alpha$	4 4	$1 + 3\alpha$ $1 + 3\alpha$	$\frac{M_{w_{\text{normal}}}}{1 + 3\alpha}$ $\frac{M_{w_{\text{normal}}}}{1 + 3\alpha}$
5.	Association of solute	Benzoic acid forming dimer in benzene	$nA \rightleftharpoons A_n$ $1-\alpha \quad \alpha$ n	$\frac{1}{n}$	$\left[1 - \left(1 - \frac{1}{n} \right) \alpha \right]$	$\frac{M_{w_{\text{normal}}}}{\left[1 - \left(1 - \frac{1}{n} \right) \alpha \right]}$
6.	General electrolyte AB_{n-1}	One mole of solute giving n ions in the solution	$AB_{n-1} \rightleftharpoons A^{n+} + (n-1)B^{\ominus}$ $1-\alpha \quad \alpha \quad (n-1)\alpha$	n	$[1 + (n-1)\alpha]$	$\frac{M_{w_{\text{normal}}}}{[1 + (n-1)\alpha]}$

Inclusion of Van't Hoff factor modifies the equation for colligative properties as follows:

Relative lowering of the vapour pressure of solvent,

$$\frac{P_1^\circ - P_1}{P_1^\circ} = i \cdot \frac{n_2}{n_1} \text{ or } i\chi_2$$

Elevation of boiling point, $\Delta T_b = iK_b m$

Depression in freezing point, $\Delta T_f = iK_f m$

Osmotic pressure of solution, $\pi = iCRT$

2.12.1 CALCULATION OF THE EXTENT OF DISSOCIATION OR ASSOCIATION IN AN ELECTROLYTIC SOLUTION

The Van't Hoff factor may be used to calculate the extent of dissociation or association in terms of the degree of dissociation or association of a substance in a solution.

Degree of Dissociation

It is defined as the fraction of total substance that undergoes dissociation into ions.

$$\text{Degree of dissociation} = \frac{\text{Number of moles of the substance dissociated}}{\text{Total number of moles of the substance taken}}$$

Suppose a molecule of an electrolyte gives n ions after dissociation and α is the degree of dissociation, then at equilibrium

Number of moles of solute left undissociated = $1 - \alpha$

Number of moles of ions formed = $n\alpha$

Total number of moles of particles = $1 - \alpha + n\alpha$

\therefore Van't Hoff factor,

$$\begin{aligned} i &= \frac{\text{Observed number of moles of solute}}{\text{Normal number of moles of solute}} \text{ or} \\ &= \frac{\text{Total number of moles at equilibrium}}{\text{Initial number of moles}} \\ &= \frac{1 - \alpha + n\alpha}{1} \end{aligned}$$

$$\text{or } \alpha = \frac{i - 1}{n - 1}$$

$$\text{But } i = \frac{\text{Normal (calculated) molar mass}}{\text{Observed molar mass}} = \frac{Mw_{(\text{calculated})}}{Mw_{(\text{observed})}}$$

$$\text{or } i = \frac{Mw_c}{Mw_o}$$

$$\therefore \alpha = \frac{Mw_c - Mw_o}{Mw_o (n - 1)}$$

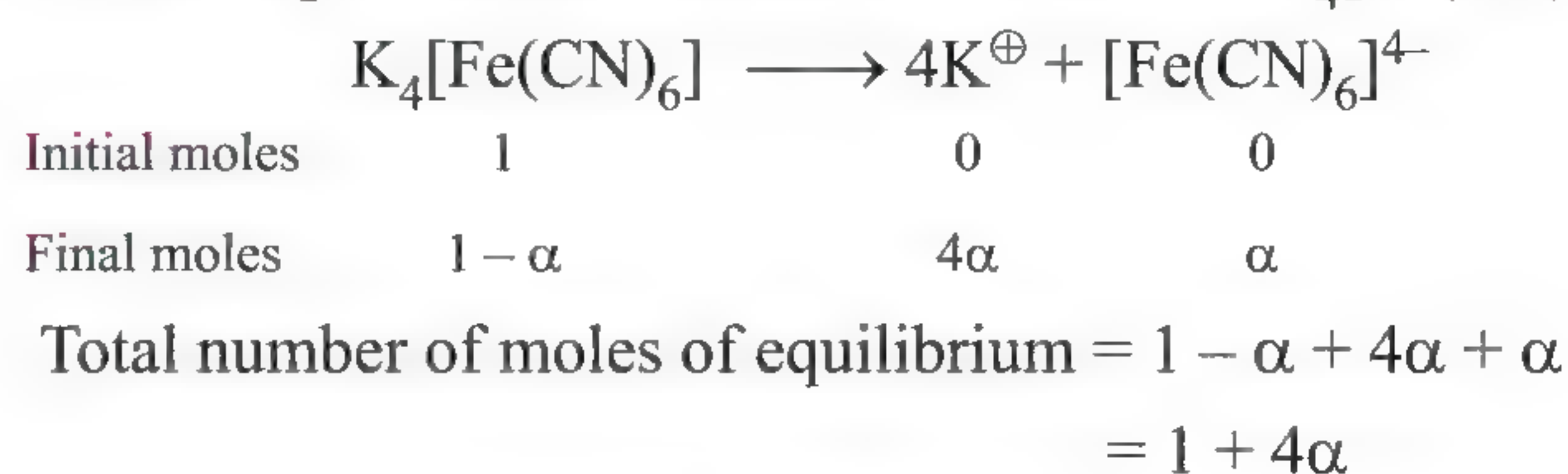
Thus, knowing the value of observed molar mass and n , the degree of dissociation, α can be calculated.

Alternative method for the calculation of Van't Hoff factor in dissociation

Let α is the degree of dissociation.

$$\therefore i = (\text{number of ions after association} \times \alpha) + (1 - \alpha)$$

For example, let consider 50% ionization of $K_4[Fe(CN)_6]$.



$$\begin{aligned} \therefore i &= \frac{\text{Total number of moles at equilibrium}}{\text{Initial moles}} = \frac{1 + 4\alpha}{1} \\ &= 1 + 4 \times 0.5 = 1 + 2 = 3 \end{aligned}$$

Alternate method

$$\begin{aligned} i &= [\text{Number of ions after ionization} \times \alpha] + (1 - \alpha) \\ &= (5 \times 0.5) + (1 - 0.5) \\ &= 2.5 + 0.5 = 3 \end{aligned}$$

Degree of Association

It is defined as the fraction of total number of molecules which combine to form associated molecules.

$$\text{Degree of association} = \frac{\text{Number of moles of the substance associated}}{\text{Total number of moles of the substance taken}}$$

Suppose n molecules of the solute associate to form the associated molecule An and α is degree of association, then

$$nA = An$$

The concentration of species at equilibrium are:

Number of moles of solute left unassociated = $1 - \alpha$

Number of moles of solute after association = α/n

Total number of moles after association = $1 - \alpha + \alpha/n$

$$\begin{aligned} \therefore \text{Van't Hoff factor } (i) &= \frac{\text{Observed number of moles of solute}}{\text{Normal number of moles of solute}} \text{ or} \\ &= \frac{\text{Total number of moles at equilibrium}}{\text{Initial number of moles}} \\ &= \frac{1 - \alpha + (\alpha/n)}{1} \end{aligned}$$

$$i = 1 + \alpha(1/n - 1)$$

$$\text{or } \alpha = -\frac{i - 1}{(1/n) - 1}$$

$$\text{Also, } i = -\frac{\text{Normal (calculate) molar mass}}{\text{Observed molar mass}} = \frac{Mw_c}{Mw_o}$$

$$\therefore 1 - \alpha + \frac{\alpha}{n} = \frac{Mw_c}{Mw_o}$$

$$\text{or } 1 - \frac{Mw_c}{Mw_o} = \alpha - \frac{\alpha}{n}$$

$$\text{or } \frac{Mw_o - Mw_c}{Mw_o} = \alpha \left(1 - \frac{1}{n}\right) = \alpha \left(\frac{n-1}{n}\right)$$

$$\therefore \alpha = \frac{Mw_o - Mw_c}{Mw_c} \left(\frac{n}{n-1}\right)$$

Molality (m) of acetic acid,

$$= \frac{W_2 \times 1000}{Mw_2 \times W_1} \left[\begin{array}{l} 1 \text{ L of H}_2\text{O} = 1000 \text{ g} \\ \text{Since } d_{\text{H}_2\text{O}} = 1 \text{ g mL}^{-1} \end{array} \right]$$

$$= \frac{0.636 \times 1000}{60 \times 1000} = 0.0106 \text{ mol kg}^{-1}$$

Substituting the values in the equation

$$\Delta T_f = iK_f \times m$$

$$0.0205 \text{ K} = i \times 1.86 \text{ K kg}^{-1} \text{ mol}^{-1} \times 0.0106 \text{ mol kg}^{-1}$$

$$\therefore i = 1.041$$

Acetic acid is a weak electrolyte and dissociates in water.

Let x is the degree of dissociation of acetic acid. Thus,



Total number of moles at equilibrium

$$= c(1-x) + cx + cx = c(1+x)$$

$$\therefore i = \frac{\text{Number of moles at equilibrium}}{\text{Number of moles initially}} = \frac{c(1+x)}{c}$$

$$\therefore 1.041 = 1 + x \Rightarrow x = 0.041$$

$$\therefore K_a = \frac{[\text{CH}_3\text{COO}^{\ominus}][\text{H}^{\oplus}]}{[\text{CH}_3\text{COOH}]} = \frac{cx \times cx}{c(1-x)}$$

$$= \frac{0.0106m \times 0.041 \times 0.041}{(1.00 - 0.041)}$$

$$= 1.86 \times 10^{-5}$$

ILLUSTRATION 2.182

The freezing point depression of $0.001 \text{ m K}_x[\text{Fe}(\text{CN})_6]$ is $7.10 \times 10^{-3} \text{ K}$. Determine the value of x . Given, $K_f = 1.86 \text{ K kg mol}^{-1}$ for water.

Sol. $\Delta T_f = i \times K_f \times m$

$$7.10 \times 10^{-3} = i \times 1.86 \times 0.001$$

$$i = 3.817$$

$$\alpha = \frac{i-1}{n-1}$$

$$1 = \frac{3.817-1}{(x+1)-1}$$

$$x = 2.817 \approx 3$$

\therefore Molecular formula of the compound is $\text{K}_3[\text{Fe}(\text{CN})_6]$.

ILLUSTRATION 2.183

A solution of non-volatile solute in water freezes at -0.80°C . The vapour pressure of pure water at 298 K is 23.51 mm Hg and K_f for water is 1.86 degree per molal. Calculate the vapour pressure of this solution at 298 K .

Sol. Depression in freezing point, $\Delta T_f = 0 - (-0.30) = 0.30$

Now, $\Delta T_f = K_f \times m$

or $m = \frac{\Delta T_f}{K_f}$

$$\therefore m = \frac{0.80}{1.86} = 0.430$$

According to Raoult's law,

$$\frac{P^\circ - P}{P^\circ} = \chi_B = \frac{n_B}{n_A + n_B},$$

or $\frac{P^\circ - P}{P^\circ} = \frac{n_B}{n_A}$ (for dilute solution)

Here, $n_B = 0.430$, $n_A = \frac{1000}{18}$; $P^\circ = 23.51$

$$\therefore \frac{23.51 - P}{23.51} = \frac{0.43 \times 18}{1000} = 0.00774$$

$$P = 23.51 - (23.51 \times 0.00774) = 23.32 \text{ mm Hg}$$

ILLUSTRATION 2.184

A 1.17% solution of NaCl is isotonic with 7.2% solution of glucose. Calculate the Van't Hoff factor of NaCl .

Sol. For isotonic solution, osmotic pressure should be same.

$$\therefore \pi_{(\text{NaCl})} = \pi_{(\text{glucose})}$$

$$iC_1RT = C_2RT$$

$$iC_1 = C_2$$

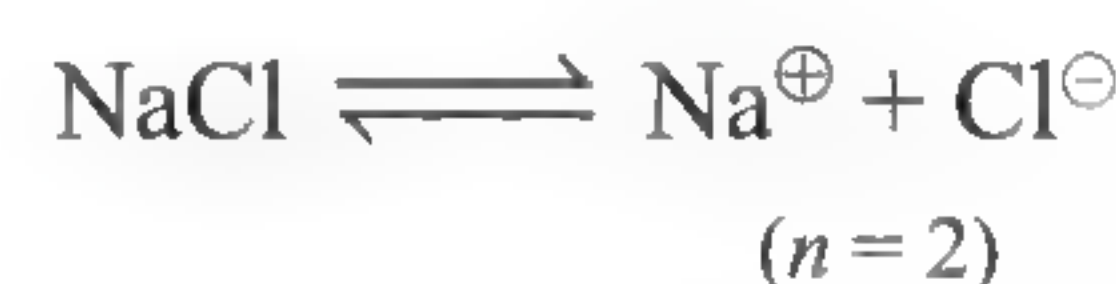
$$i \left(\frac{1.17/58.5}{V} \right) = \frac{7.2/180}{V} \Rightarrow i = \frac{7.2 \times 58.5}{1.17 \times 180} = 2$$

ILLUSTRATION 2.185

Calculate the amount of NaCl which must be added to 100 g water so that the freezing point, depressed by 2 K . For water $K_f = 1.86 \text{ K kg mol}^{-1}$.

Sol. NaCl is a strong electrolyte. It is completely dissociated in solution.

Degree of dissociation, $\alpha = 1$



$$\begin{aligned} \text{Number of particles after dissociation} &= 1 + (n-1)\alpha \\ &= 1 + (2-1) \times 1 \\ &= 2 \end{aligned}$$

$$\frac{\Delta T_{\text{obs}}}{\Delta T_{\text{theo}}} = \frac{\text{Number of particles after dissociation}}{\text{Number of particles when there is no dissociation}}$$

$$\frac{2}{\Delta T_{\text{theo}}} = 2$$

or $\Delta T_{\text{theo}} = 1$

Let $W \text{ g}$ of NaCl be dissolved in 100 g of water.

So $\Delta T_{\text{theo}} = \frac{1000 \times K_f \times W_2}{W_1 \times Mw_1}$

or $W_2 = \frac{\Delta T_{\text{theo}} \times W_1 \times Mw_1}{1000 \times K_f} = \frac{1 \times 100 \times 58.5}{1000 \times 1.86} = 3.145 \text{ g}$

ILLUSTRATION 2.186

0.002 molar solution of NaCl having degree of dissociation of 90% at 27°C has osmotic pressure equal to

- a. 0.94 bar b. 9.4 bar c. 0.094 bar d. 9.4×10^{-4} bar

Sol.

$$\text{c. } \alpha = \frac{i-1}{n-1}$$

$$0.9 = \frac{i-1}{2-1}; i = 1.9$$

Alternate method to calculate (i)

$$\begin{aligned} i &= (\text{Number of ions} \times \alpha) + (1 - \alpha) \\ &= (2 \times 0.9) + (1 - 0.9) \quad [\alpha = 90\% \text{ or } 0.9] \\ &= 1.8 + 0.1 = 1.9 \end{aligned}$$

$$\begin{aligned} \pi &= iCRT \\ &= 1.9 \times 0.002 \times 0.082 \times 300 \\ &\approx 0.094 \text{ bar} \end{aligned}$$

ILLUSTRATION 2.187

Osmotic pressure of 0.1 M aqueous solution of MgCl_2 at 300 K is 4.92 atm. What will be the percentage ionization of the salt?

- a. 49% b. 59% c. 79% d. 69%

Sol.

$$\begin{aligned} \text{a. } \pi &= iCRT \\ 4.92 &= i \times 0.1 \times 0.0821 \times 300 \\ i &= 1.99 \\ \alpha &= \frac{i-1}{n-1} = \frac{1.99-1}{3-1} = \frac{0.99}{2} = 0.49 \end{aligned}$$

Percentage of ionization = 49%

ILLUSTRATION 2.188

The Van't Hoff factor of Hg_2Cl_2 in its aqueous solution will be (Hg_2Cl_2 is 80% ionized in the solution)

- a. 1.6 b. 2.6 c. 3.6 d. 4.6

Sol. $\text{b. } \text{Hg}_2\text{Cl}_2 \rightleftharpoons \text{Hg}_2^{2+} + 2\text{Cl}^-$

$$\begin{aligned} n &= 3 \\ \alpha &= \frac{i-1}{n-1} \Rightarrow 0.8 = \frac{i-1}{3-1} \Rightarrow i = 2.6 \end{aligned}$$

Alternate method to calculate (i)

$$\begin{aligned} i &= (\text{Number of ions} \times \alpha) + (1 - \alpha) \\ &= (3 \times 0.8) + (1 - 0.8) \quad [\alpha = 80\% \text{ or } 0.8] \\ &= 2.4 + 0.2 = 2.6 \end{aligned}$$

ILLUSTRATION 2.189

A certain substance A tetramerizes in water to the extent of 80%. A solution of 2.5 g of A in 100 g of water lowers the freezing point by 0.3°C. The molar mass of A is (K_f for water = 1.86 K m^{-1}).

- a. 124 b. 32 c. 50 d. 62

Sol.

$$\begin{aligned} \text{d. } \alpha &= \frac{1-i}{1-\frac{1}{n}} \\ 0.8 &= \frac{1-i}{1-\frac{1}{4}} \Rightarrow i = 0.4 \end{aligned}$$

Given that $4A \longrightarrow A_4$

Alternate method to calculate (i)

$$\begin{aligned} i &= (\text{Number of ions} \times \alpha) + (1 - \alpha) \\ &= \left(\frac{1}{4} \times 0.8 \right) + (1 - 0.8) \quad [\alpha = 80\% \text{ or } 0.8] \\ &= 0.2 + 0.2 = 0.4 \\ \Delta T &= iK_f \times m \end{aligned}$$

$$0.3 = 0.4 \times 1.86 \times \frac{W_B \times 1000}{Mw_B \times W_A}$$

$$0.3 = 0.4 \times 1.86 \times \frac{2.5 \times 1000}{Mw_B \times 100} \Rightarrow Mw_B = 62$$

ILLUSTRATION 2.190

When cells of skeletal vacuoles of a frog were placed in a series of NaCl solutions of different concentration solution at 25°C, it was observed microscopically that they remained unchanged in 0.7% solution, shrank in a more concentrated and swelled in more dilute solutions. Water freezes from the 0.7% salt solutions at -0.406°C . What is the osmotic pressure of the cell cytoplasm at 25°C. ($K_f = 1.86 \text{ K kg mol}^{-1}$)

Sol. $\Delta T_f = K_f \times i \times C_m$

$$= K_f \times (1 + \alpha) \times \frac{W}{m} \times \frac{1000}{W \text{ (in g)}}$$

$$\therefore 0.406 = 1.86 \times (1 + \alpha) \times \frac{0.7}{58.5} \times \frac{1000}{99.3}$$

$$\therefore 1 + \alpha = \frac{0.4 \times 58.5 \times 100}{1.86 \times 0.7 \times 1000}$$

Assuming dilute solution

$$100 \text{ g H}_2\text{O} = 100 \text{ mL H}_2\text{O} = 0.1 \text{ L solutions}$$

$$\begin{aligned} \pi &= i \times \frac{n_2}{V} \times RT = (1 + \alpha) \times \frac{W_2}{Mw_2} \times \frac{1}{V} \times RT \\ &= \frac{0.406 \times 58.5 \times 100}{1000 \times 1.86 \times 0.7} \times \frac{0.7}{58.5} \times \frac{1}{0.1} \times 0.082 \times 298 \\ &= 5.34 \text{ atm} \end{aligned}$$

ILLUSTRATION 2.191

A saturated solution of $\text{Mg}(\text{OH})_2$ has a vapour pressure of 759.5 mm at 373 K. Calculate the solubility and K_{sp} of $\text{Mg}(\text{OH})_2$. (Assume molarity equals molality)

Sol. $P_s = 759.5 \text{ mm}$

$$P_{\text{H}_2\text{O}}^\circ = 760 \text{ mm at } 373 \text{ K}$$

$$\frac{\Delta P}{P^\circ} = \frac{0.5}{760} = i\chi_2$$

$$\therefore i\chi_2 = 6.5 \times 10^{-4} \quad (i = 3)$$

$$\chi_2 = 2.16 \times 10^{-4}$$

Find molality \approx molarity

$$m = \frac{\chi_B \times 1000}{(1 - \chi_B) \times M_{W_1}} = 0.012 \text{ mol kg}^{-1}$$



$$i = 3$$

$$S = 0.012 \text{ mol L}^{-1}$$

$$\begin{aligned} K_{\text{sp}} &= 4S^3 \\ &= 4 \times (0.012)^3 \\ &= 6.8 \times 10^{-6} \end{aligned}$$

ILLUSTRATION 2.192

The freezing point of an aqueous solution of KCN containing $0.1892 \text{ mol kg}^{-1}$ was found to be -0.704°C . On adding 0.095 mol of Hg(CN)_2 , the freezing point of the solution was found to be -0.530°C . If the complex formation takes place according to the following equation:



What is the formula of the complex? [$K_f(\text{H}_2\text{O})$ is $1.86 \text{ K kg mol}^{-1}$]

Sol. For KCN, $i = 1 + \alpha$, where α = degree of dissociation

$$\Delta T_f = K_f \times i \times \text{molarity}$$

$$0.704 = 1.86 \times i \times 0.1892$$

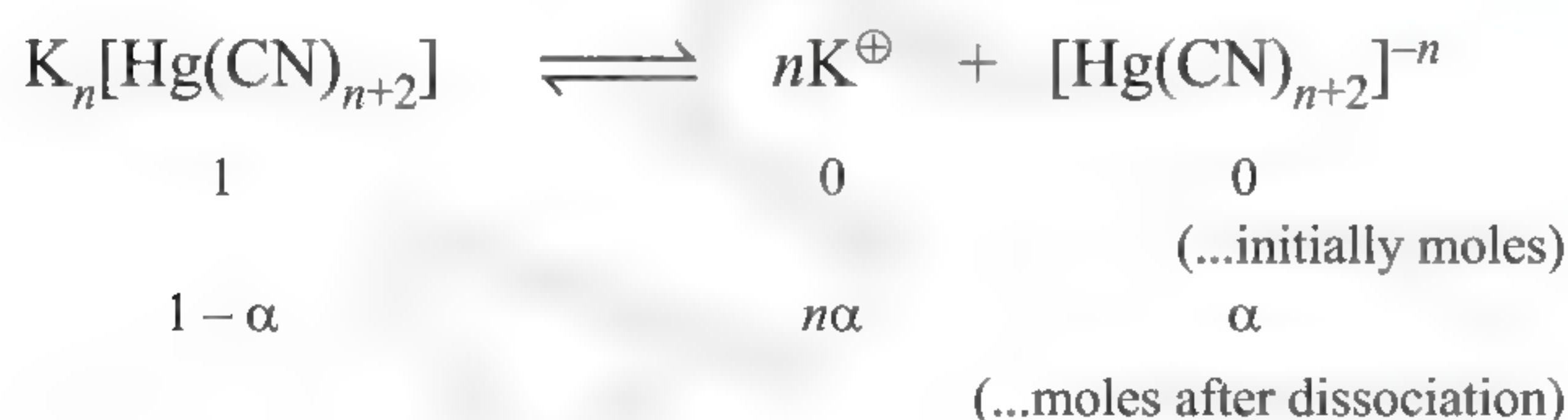
$$i = \frac{0.704}{1.86 \times 0.1892} = 2$$

$$\text{or } 1 + \alpha = 2$$

$$\therefore \alpha = 1 \text{ indicates } 100\% \text{ ionization of KCN.}$$

$$\text{Now, } \Delta T_f = (\text{of the complex}) = 0.530^\circ\text{C}$$

$$\text{Molality of } \text{Hg(CN)}_2 = 0.095 \text{ mol kg}^{-1} = 0.095 \text{ m}$$



$$\text{Here, } i = (1 - \alpha) + n\alpha + \alpha = 1 + n\alpha$$

$$\therefore \alpha = 1$$

$$\therefore i = 1 + n$$

$$\Delta T_f = K_f \times i \times \text{molality}$$

$$\Rightarrow 0.503 = 1.86 \times i \times 0.095$$

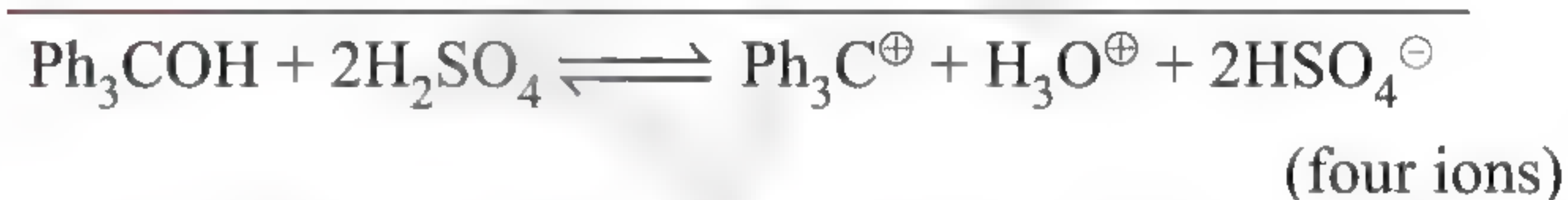
$$\Rightarrow i \approx 3$$

$$1 + n = 3 \text{ or } n = 2$$

Hence, the complex is $\text{K}_2[\text{Hg(CN)}_4]$.

ILLUSTRATION 2.193

One mole of triphenyl methanol lowers the freezing point of 1000 g of 100% sulphuric acid twice as much as one mole of methanol. Why?



Since the number of ions are doubled in Ph_3COH and so depression is two times more for the same number of moles of each.

ILLUSTRATION 2.194

A 0.025 m solution of monobasic acids has a freezing point of -0.060°C . What are K_a and $\text{p}K_a$ of the acid? ($K_f = 1.86^\circ\text{C}$)



$$\therefore i = 1.29$$



1	0	0
$(1 - \alpha)$	α	α

$$\therefore i = 1 - \alpha + \alpha + \alpha = 1 + \alpha$$

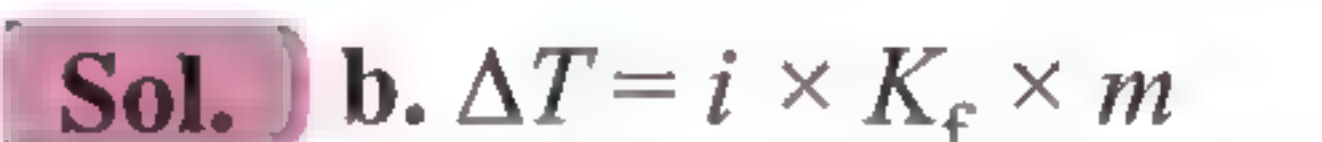
$$\therefore \alpha = 0.29$$

$$K_a = \frac{C\alpha^2}{1 - \alpha} = \frac{0.025 \times (0.29)^2}{(1 - 0.29)} = 3 \times 10^{-3} \Rightarrow \text{p}K_a = 2.5$$

ILLUSTRATION 2.195

A 0.2 molal solution of KCl freezes at -0.68°C . If K_f for H_2O is 1.86 , the degree of dissociation of KCl is

- a. 85% b. 83% c. 65% d. 90%



$$0.68 = i \times 1.86 \times 0.2$$

$$i = 1.83$$

$$\alpha = \frac{i - 1}{n - 1} = \frac{1.83 - 1}{2 - 1} = 0.83$$

$$\text{Ionization} = 83\%$$

ILLUSTRATION 2.196

A mixture of 0.1 mol of Na_2O and 0.1 mol of BaO is dissolved in 1000 g of H_2O . Calculate the vapour pressure of solution at 373 K .

Sol. Na_2O and BaO both are ionic compounds and are completely ionized to give 3 and 2 ions, respectively,



Note: Moles of $\text{H}_2\text{O} = \frac{1000}{18} = 55.5$

$$\therefore \frac{P^\circ - P_s}{P^\circ} = i\chi_{\text{Na}_2\text{O}} + i\chi_{\text{BaO}}$$

$$\frac{760 - P_s}{760} = 3 \times \frac{0.1}{0.1 + 0.1 + 55.5} + 2 \times \frac{0.1}{0.1 + 0.1 + 55.5}$$

$$\therefore P_s = 753.21 \text{ mm Hg}$$

Alternatively

Total number of ions = $5 \times 0.1 = 0.5$

$$\frac{P^\circ - P_s}{P_s} = \frac{n_2}{n_1} = \frac{0.5}{55.5} = 0.009$$

$$\frac{760 - P_s}{P_s} = 0.009$$

Solve for $P_s \Rightarrow 753.21 \text{ mm Hg}$.

ILLUSTRATION 2.197

1575.2 g of $\text{C}_6\text{H}_5\text{OH}$ (phenol) is dissolved in 960 g of a solvent of $K_f = 14 \text{ K kg mol}^{-1}$. If the depression in freezing point is 7 K, then find the percentage of phenol that dimerizes.



$$1 - \alpha \qquad \qquad \alpha/2$$

$$i = 1 - \alpha + \frac{\alpha}{2} = \frac{\Delta T_f}{K_f \cdot m} \Rightarrow \alpha = 0.8$$

ILLUSTRATION 2.198

Following are equimolal aqueous solutions:

a. 1 m urea

b. 1 m KCl

c. 1 m MgCl_2

d. 1 m Na_3PO_4

Arrange them in increasing

i. Boiling point

ii. Freezing point

iii. Osmotic pressure

iv. Vapour pressure

Sol. While analysing the colligative properties, if the density of the solution is not given, take the molarity of the solution same as molality and vice-versa.

In such type of questions, always assume 100% dissociation for the ionic solutes until and unless specified

Solute	Ionization	i
a. Urea	No	1
b. KCl	$\text{K}^\oplus + \text{Cl}^\ominus$	2
c. MgCl_2	$\text{Mg}^{2+} + 2\text{Cl}^\ominus$	3
d. Na_3PO_4	$3\text{Na}^\oplus + \text{PO}_4^{3-}$	4

i. Boiling point of solution

$$T_b = T_b^\circ + (\Delta T_b)$$

$$\Delta T_b = i(K_b m)$$

Thus, greater the value of i , greater the value of ΔT_b and boiling point of solution.

$$a < b < c < d$$

ii. Freezing point of solution

$$T_f = T_f^\circ - (\Delta T_f)$$

$$\Delta T_f = i(K_f m)$$

Thus, greater the value of i , greater the value of ΔT_f but smaller the value of freezing point.

$$d < c < b < a$$

iii. Osmotic pressure (π)

$$\pi = iCRT$$

Thus, greater the value of i , larger the value of osmotic pressure.

$$a < b < c < d$$

iv. Vapour pressure of solution

$$\frac{\Delta P}{P_A^\circ} = i\chi_B \text{ or } \frac{\Delta P}{P_A^\circ} = i \frac{n_B}{n_A + n_B} \approx \frac{n_B}{n_A}$$

Thus, greater the value of i , greater the value of ΔP .

Hence, smaller the value of vapour pressure of solution.

$$d < c < b < a$$

ILLUSTRATION 2.199

To 250 mL of water, x g of acetic acid is added. If 11.5% of acetic acid is dissociated, the depression in freezing point comes out 0.416. What will be the value of x if $K_f(\text{water}) = 1.86 \text{ K kg}^{-1} \text{ mol}^{-1}$ and density of water is 0.997 g mL^{-1} .

Sol. Given that: $W_2 = x \text{ g}$; $\Delta T_f = 0.416$; $\alpha = 0.115$

$$\alpha = \frac{i - 1}{n - 1}$$

So, $i = 1.115$

$$\Delta T_f = i \times m \times K_f$$

$$\Delta T_f = i \times \frac{W_2 \times 1000 \times K_f}{M_{W_2} \times W_1}$$

$$0.416 = 1.115 \times \frac{x \times 1000 \times 1.86}{60 \times 249.25} \quad [W_2 = x \text{ g}]$$

$$x = \frac{0.416 \times 60 \times 249.25}{1.115 \times 1000 \times 1.86} = 3 \text{ g}$$

ILLUSTRATION 2.200

A 250-mL water solution containing 8.19 g of sodium chloride at 300 K is separated from pure water by means of a semi-permeable membrane. The pressure that must be applied above this solution in order to just prevent osmosis is ($R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$)

a. 13.80 atm

b. 27.58 atm

c. 23.34 atm

d. 9.80 atm

Sol. b. $\pi = i \times C \times R \times T$ [for NaCl, $i = 2$]

$$= 2 \times \frac{8.19}{58.5} \times \frac{1000}{250} \times 0.0821 \times 300 = 27.58 \text{ atm}$$

ILLUSTRATION 2.201

Calculate the osmotic pressure of a solution containing 0.02 mol of NaCl and 0.03 mol of glucose in 500 mL at 27°C .

Sol. $C_{\text{effective}} = i_{\text{NaCl}} (= 2) \times C_{\text{NaCl}} + i_{\text{Glucose}} (= 1) \times C_{\text{Glucose}}$

$$= \left(2 \times \frac{0.02}{500/1000} + 1 \times \frac{0.03}{500/1000} \right) \text{M}$$

$$= 0.14 \text{ M}$$

$$\Rightarrow \pi = C_{\text{eff}} RT = 0.14 \times 0.082 \times 300 \text{ atm} = 3.44 \text{ atm}$$

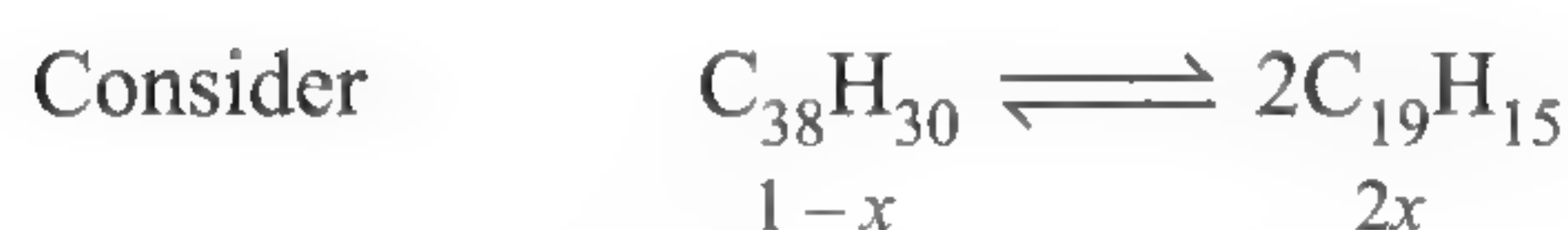
ILLUSTRATION 2.202

When dissolved in benzene, a compound $\text{C}_{38}\text{H}_{30}$ partially dissociates by the following equation:

$\text{C}_{38}\text{H}_{30} \rightleftharpoons 2\text{C}_{19}\text{H}_{15}$. 25.6 g of $\text{C}_{38}\text{H}_{30}$ is dissolved in 400 g of benzene, the freezing point is lowered by 0.680°C . What percentage of $\text{C}_{38}\text{H}_{30}$ molecules have dissociated? ($K_f = 4.9$)

Sol. $\Delta T_f = iK_f m$

$$i = \frac{\Delta T_f}{K_f \left(\frac{W_B}{\frac{Mw_B}{W_A} \times 1000} \right)} = \frac{0.68}{4.9 \left(\frac{25.6}{\frac{486}{400} \times 1000} \right)} = 1.0538$$



$$\text{Total moles} = 1 - x + 2x = 1 + x$$

$$i = \frac{\text{Total moles}}{\text{Initial moles}} = \frac{1+x}{1}$$

$$\Rightarrow 1.0538 = \frac{1+x}{1} \Rightarrow x = 0.0538$$

$$\Rightarrow \text{Percentage dissociation} = 5.38\%$$

ILLUSTRATION 2.203

Find the Van't Hoff factor of

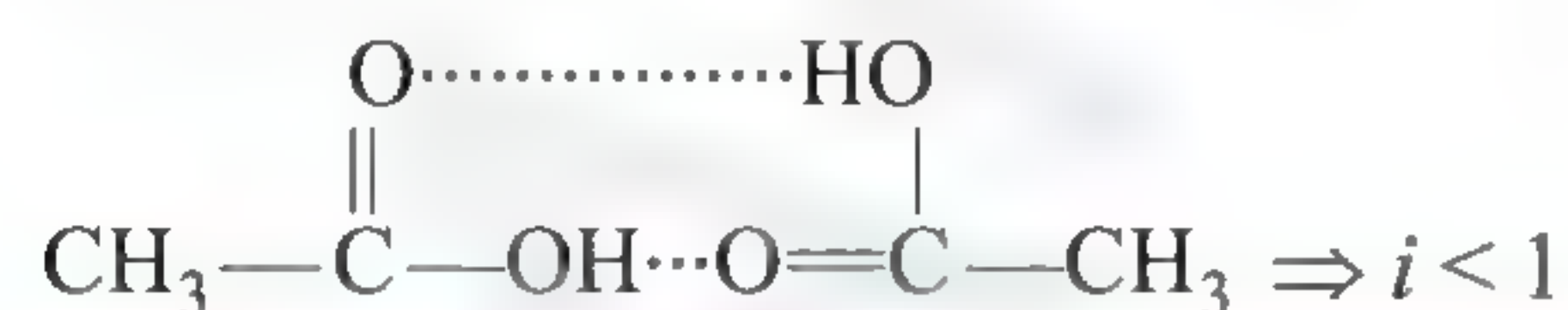
- CH_3COOH in H_2O
- CH_3COOH in benzene

Sol.

- CH_3COOH in water dissociates (as a weak acid)



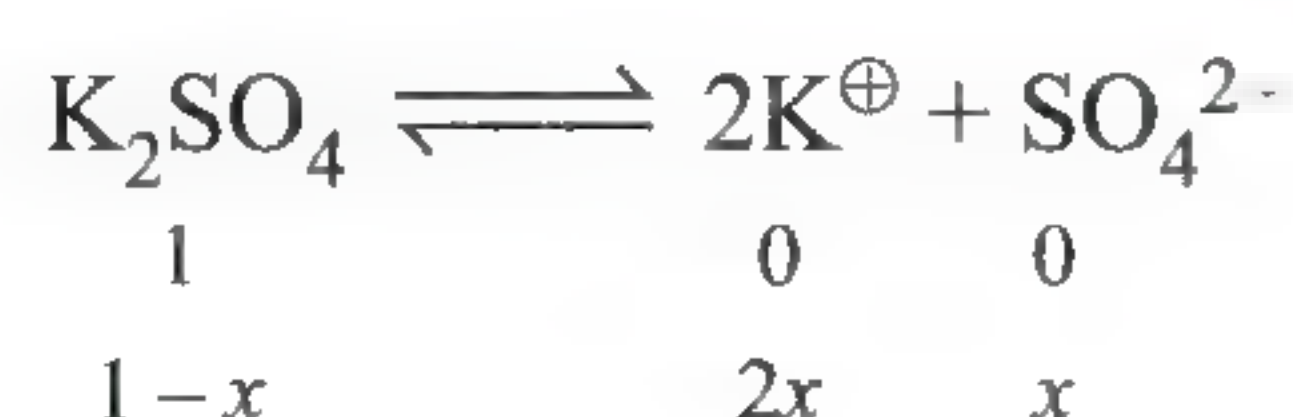
- CH_3COOH in benzene (i.e., non-polar solvent) associates to form a dimer.

**ILLUSTRATION 2.204**

A 0.1 M solution of potassium sulphate K_2SO_4 is dissolved to the extent of 80%. What would be its osmotic pressure at 27°C ?

Sol. Use the result: $\pi = iCRT$

Calculation of i :



$$\text{Total moles} = 1 - x + 2x + x = 1 + 2x$$

$$i = \frac{1+2x}{1} = \frac{1+2 \times 0.8}{1} = 2.6$$

$$\pi = 2.6 \times (0.1 \times 0.0821 \times 300) = 6.40 \text{ atm}$$

ILLUSTRATION 2.205

Van't Hoff factors of aqueous solutions of X, Y, and Z are 2.8, 1.8, and 3.5, respectively. Which of the following statement(s) is(are) correct?

- BP: $X < Y < Z$
- FP: $Z < X < Y$
- Osmotic pressure: $X = Y = Z$
- VP: $Y < X < Z$

Sol. Observed colligative property = $i \times$ Normal colligative property

- Elevation in BP follows the order: $Y < X < Z$

$$\Rightarrow \text{BP following the order: } Y < X < Z$$

- Depression in FP follows the order:

$$Y < X < Z \quad (T_f = T_f^\circ - \Delta T_f)$$

$$\Rightarrow \text{FP following the order: } Z < X < Y$$

- Osmotic pressure follows the order: $Y < X < Z$

- Relative lowering in the VP follows:

$$Y < X < Z$$

$$\text{VP follows the order: } Z < X < Y$$

ILLUSTRATION 2.206

Acetic acid associates in benzene to form a dimer. 1.65 g of acetic acid when dissolved in 100 g of benzene raised the boiling point by 0.36°C . Calculate the Van't Hoff factor and degree of association of acetic acid.

$$(K_b \text{ for benzene} = 2.57^\circ\text{C m}^{-1})$$

Sol. Calculation of Van't Hoff factor:

First calculate the molecular mass from elevation in boiling point.

$$Mw_B = K_b \left(\frac{W_B}{W_A \Delta T_b} \times 1000 \right)$$

$$= 2.57 \left(\frac{1.65}{100 \times 0.36} \times 1000 \right) = 117.8$$

$$\Rightarrow i = \frac{\text{Normal molecular weight}}{\text{Observed molecular weight}} = \frac{60}{117.8} = 0.509$$

Calculation of degree of association:

Let x = degree of association



$$\begin{array}{ccc} & 1 & 0 \\ & 1-x & x/2 \end{array}$$

$$\text{Total moles} = 1 - x/2$$

$$i = \frac{\text{Total moles}}{\text{Initial moles}} = \frac{1 - x/2}{1}$$

$$\Rightarrow 0.509 = \frac{1-x/2}{1} \Rightarrow x = 0.982$$

ILLUSTRATION 2.207

The vapour pressure of benzene at 30°C is 164.88 mm of Hg. In 3 mol of benzene, when 6 g of acetic acid was dissolved, the vapour pressure of the solution became 162.04 mm of Hg. Calculate

- Van't Hoff factor
- The degree of association of acetic acid in benzene at 30°C

Sol. Using the relation for lowering in vapour pressure and considering the Van't Hoff factor (i), we have

$$\frac{\Delta P}{P_A^\circ} = i\chi_B$$

$$\Rightarrow \frac{(164.88 - 162.04)}{164.88} = i \left(\frac{0.1}{0.1 + 3} \right)$$

$$\Rightarrow i = 0.533 \text{ (i.e., } i < 1)$$

Hence, acetic acid associates in benzene



$$\Rightarrow i = 1 - \alpha/2$$

$$\Rightarrow \alpha = 2(1 - 0.533) = 0.932$$

ILLUSTRATION 2.208

The freezing point of a solution containing 0.3 g of acetic acid in 43 g of benzene reduces by 0.3°. Calculate the Van't Hoff factor.

(K_f for benzene = 5.12 K kg mol⁻¹)

Sol. The given values are

$$W_B = 0.3 \text{ g}; \quad \Delta T_f = 0.30$$

$$W_A = 43 \text{ g}; \quad \Delta K_f = 5.12 \text{ K kg mol}^{-1}$$

Now, using formula

$$M_{w_B} = \frac{K_f \times W_B \times 1000}{\Delta T_f \times W_A}$$

$$\therefore M_{w_B} = \frac{5.12 \times 0.3 \times 1000}{0.3 \times 43} = 120 \text{ g mol}^{-1}$$

Normal molar mass = 60

$$\therefore i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}} = \frac{60}{120} = 0.5$$

ILLUSTRATION 2.209

The freezing point of a 0.08 molal solution of NaHSO₄ is -0.372°C. Calculate the dissociation constant for the reaction.



K_f for water = 1.86 K m⁻¹

Sol. NaHSO₄ dissociates as:



Since the concentration of NaHSO₄ is 0.08 m

$$[\text{Na}^\oplus] = 0.08 \text{ m}; [\text{HSO}_4^\ominus] = 0.08 \text{ m}$$

Now, HSO₄[⊖] also dissociates as



If α is the degree of dissociation, then after dissociation at equilibrium

$$[\text{HSO}_4^\ominus] \rightleftharpoons 0.08(1 - \alpha)$$

$$[\text{H}^\oplus] = 0.08\alpha; [\text{SO}_4^{2-}] = 0.08\alpha$$

Total concentration of all ions (i.e., Na[⊕], H[⊕], HSO₄[⊖], and SO₄²⁻)

$$= 0.08 + 0.08(1 - \alpha) + 0.08\alpha + 0.08\alpha$$

$$= 0.16 + 0.08\alpha$$

$$\therefore \text{Van't Hoff factor, } i = \frac{\text{Observed moles of solute}}{\text{Normal moles of solute}}$$

$$= \frac{0.16 + 0.08\alpha}{0.08} = 2 + \alpha$$

$$\text{Now, } \Delta T_f = iK_f \times m$$

$$= i \times 1.86 \times 0.088 = 0.1488i$$

$$\text{or } 0.372 = 0.1488i$$

$$\therefore i = \frac{0.372}{0.1488} = 2.5$$

$$\text{Thus, } 2 + \alpha = 2.5 \text{ or } \alpha = 0.5$$

Dissociation constant for the reaction is

$$K = \frac{[\text{H}^\oplus][\text{SO}_4^{2-}]}{[\text{HSO}_4^\ominus]}$$

$$[\text{H}^\oplus] = 0.08 \times 0.5 = 0.04$$

$$[\text{HSO}_4^\ominus] = 0.08 \times (1 - 0.5) = 0.04$$

$$[\text{SO}_4^{2-}] = 0.08 \times 0.5 = 0.04$$

$$\therefore K = \frac{(0.04) \times (0.04)}{(0.04)} = 4 \times 10^{-2}$$

ILLUSTRATION 2.210

Which of the following is (are) correct statements?

- 0.1 M CaCl₂ has higher boiling point than 0.1 M NaCl.
- 0.05 M Al₂(SO₄)₃ has higher freezing point than 0.1 M K₃[Fe(CN)₆].
- 0.1 M glucose exerts higher osmotic pressure than 0.08 M CH₃COOH (25% dissociated).
- Vapour pressure of 0.05 M urea solution is greater than that of 0.05 M KCl solution.

The correct choice is

- a. i, iii b. ii, iv c. i, ii, iii d. i, ii, iv

Sol.

- d. T_b is higher if im is higher. T_f is higher if im is lower.
 π is higher if im is higher. VP is higher if im is lower.
 CaCl₂: $im = 3 \times 0.1$; Al₂(SO₄)₃: $im = 5 \times 0.05$;
 Glucose: $im = 1 \times 0.1$; NaCl: $im = 2 \times 0.1$;

$K_3[Fe(CN)_6]$: $im = 4 \times 0.1$;

CH_3COOH : $im = (1 + \alpha)m = 1.25 \times 0.08 = 0.1$

Urea: $im = 1 \times 0.05$; KCl : $im = 2 \times 0.05 = 0.1$

ILLUSTRATION 2.211

Under what conditions Van't Hoff factor (i) is

(a) equal to unity, (b) less than 1, and (c) greater than 1. Explain your answer.

Sol.

- When the solute does not undergo any dissociation or association in the solution, i.e., for non-electrolyte solutes.
- When the solute undergoes association in the solution.
- When the solute undergoes dissociation in the solution.

ILLUSTRATION 2.212

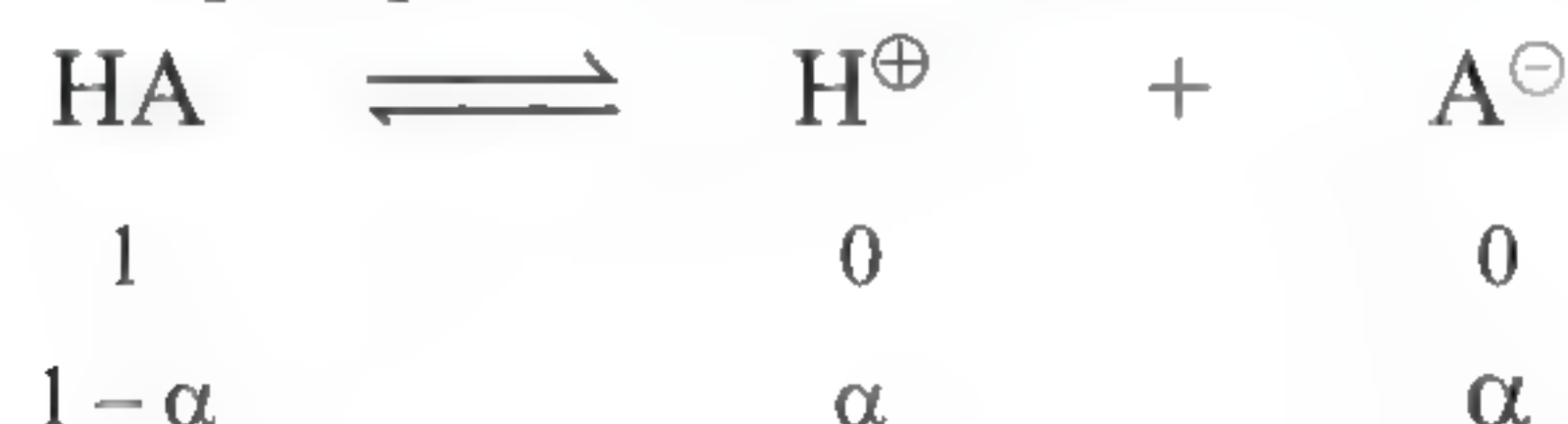
The freezing point of 0.20 M solution of weak acid HA is 272.5 K. The molality of the solution is $0.263 \text{ mol kg}^{-1}$. Find the pH of the solution on adding 0.25 M sodium acetate solution.

K_f of water = 1.86 K m^{-1}

Sol. $\Delta T_f = (273 - 272.5) = 0.5 \text{ K}$

$$\Delta T_f = iK_f m$$

$$\therefore i = \Delta T_f / K_f m = 0.5 / 1.86 \times 0.263 = 1.022$$



$$i = 1 + \alpha$$

$$1.022 = 1 + \alpha \Rightarrow \alpha = 0.022$$

$$K_a = C\alpha^2 = 0.2 \times (0.022)^2 = 9.6 \times 10^{-5}$$

$$\Rightarrow pK_a = 4.0177$$

On adding 0.25 M NaA, buffer is formed

$$\therefore [\text{Salt}] = 0.25 \text{ M}, [\text{Acid}] = 0.2 \text{ M}$$

$$\begin{aligned} \text{pH} &= pK_a + \log [\text{Salt}/\text{Acid}] = 4.0177 + \log(0.25/0.2) \\ &= 4.0177 + 0.0969 = 4.1146 \end{aligned}$$

ILLUSTRATION 2.213

Calculate the Van't Hoff factor (i) for the following if:

- 100% ionization or association takes place
- 50% ionization or association takes place

- | | | | |
|---------------|--------------|------------|--------------|
| a. S | b. Se | c. Te | d. P |
| e. As | f. Sb | g. B | h. $AlCl_3$ |
| i. Hg_2Cl_2 | j. $HgCl_2$ | k. Be_2C | l. Al_4C_3 |
| m. CaC_2 | n. Mg_2C_3 | | |

Sol.

i. (a, b, c)

S, Se, and Te exist as S_8 , Se_8 , and Te_8 molecules. So association takes place.



$$i = \frac{1}{8}$$

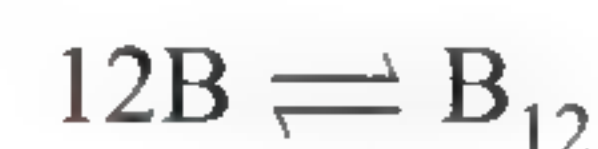
(d, e, f)

P, As, and Sb exist as P_4 , As_4 , and Sb_4 molecules, so association takes place.



$$i = \frac{1}{4}$$

g. B exists as B_{12} molecule (icosahedron structure, 12 corners, and 20 faces), association takes place.



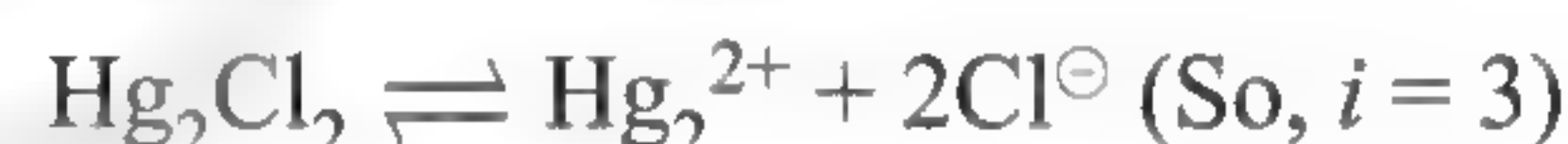
$$i = \frac{1}{12}$$

h. $AlCl_3$ exists as dimer in non-polar solvent, so association takes place.



$$i = \frac{1}{2}$$

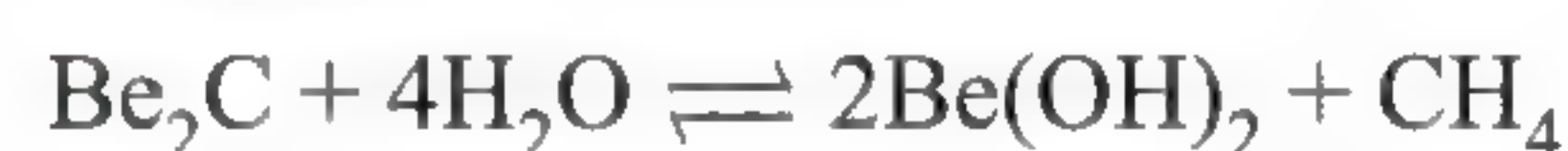
i. Hg_2Cl_2 (calomel) ionizes to give Hg_2^{2+} (mercurous ion) and $2Cl^-$ ions



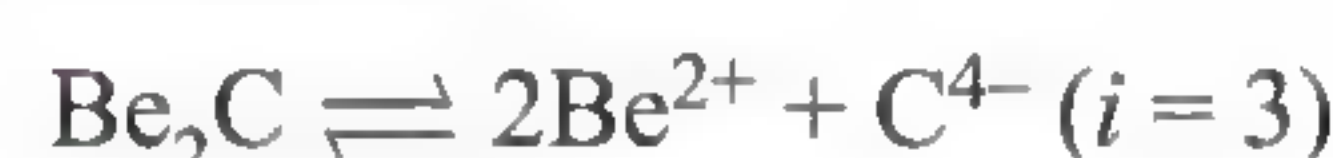
j. $HgCl_2$ (corrosive sublimate) is a covalent compound and does not ionize. So $i = 1$.

Hg_2Cl_2 is poisonous and antidote is white of an egg.

(k, l) Be_2C and Al_4C_3 in H_2O gives CH_4 gas, so it contains C^{4-} methinide ion.



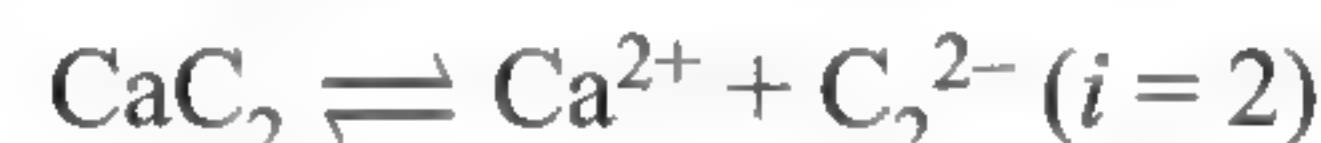
Hence, Be_2C and Al_4C_3 ionizes in solution as follows:



m. CaC_2 gives $(CH \equiv CH)$ gas with H_2O . So it contains $(C^{\ominus} \equiv C^{\ominus} \text{ or } C_2^{2-} \text{ ion})$



So CaC_2 ionizes in solution as follows:

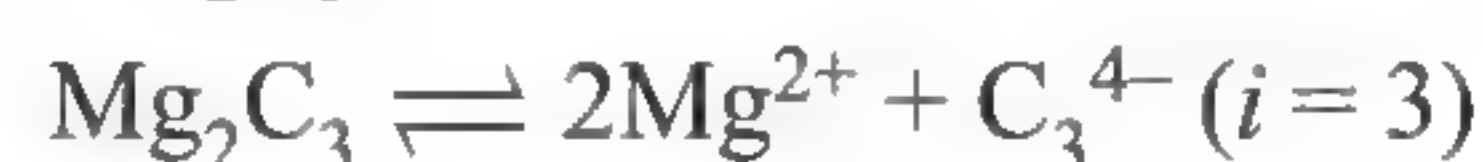


n. Mg_2C_3 gives $(CH_3 - C \equiv CH)$ gas with H_2O .

So, it contains $CH_3C \equiv C^{\ominus} \text{ or } C_3^{4-} \text{ ions}$

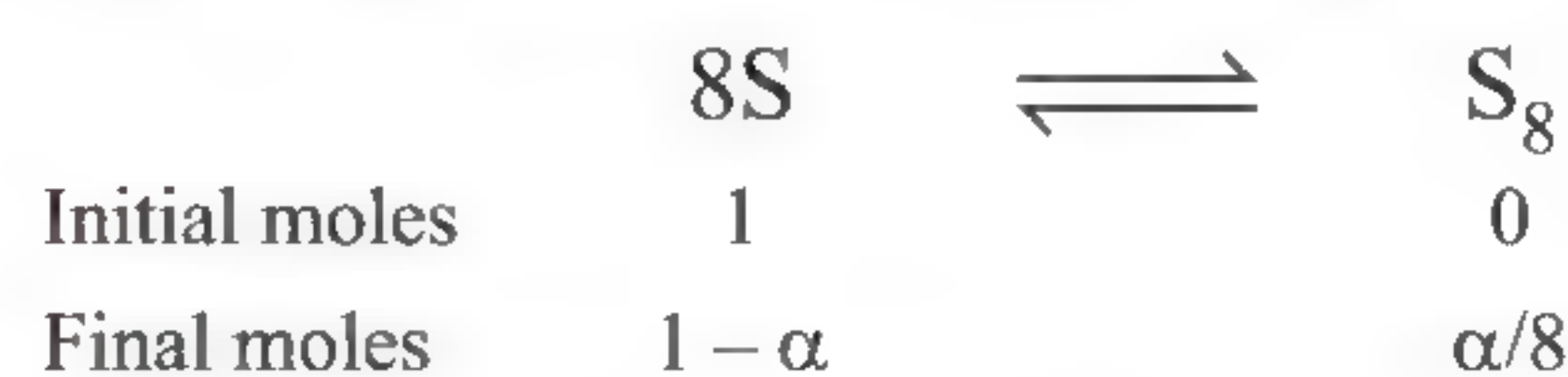


Mg_2C_3 ionizes in solution as follows:



ii. (a, b, c)

For 50% association (α) = 50% or 0.5.



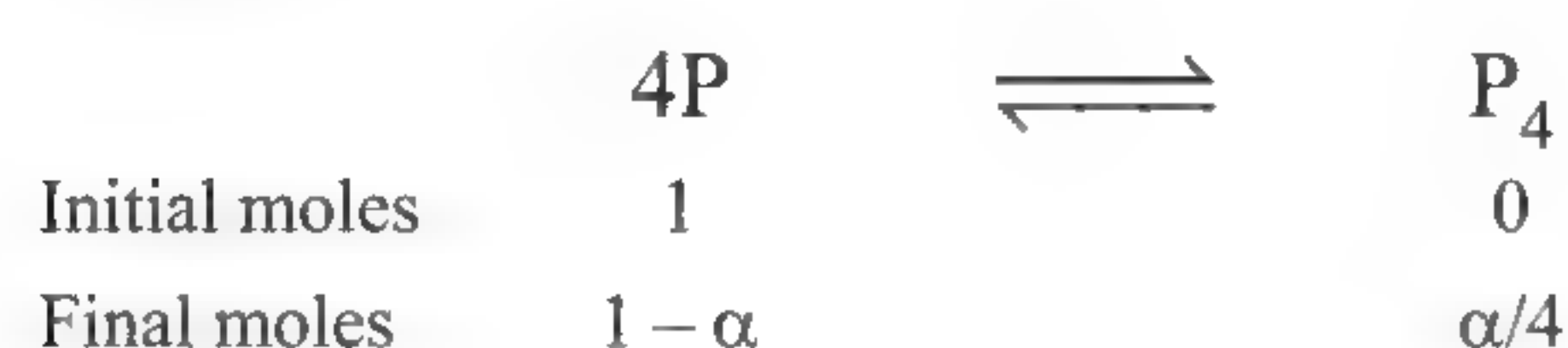
$$\text{Total moles at equilibrium} = 1 - \alpha + \frac{\alpha}{8}$$

$$i = \frac{\text{Total moles}}{\text{Initial moles}}$$

$$\begin{aligned}
 &= \frac{1 - \alpha + \frac{\alpha}{8}}{1} \\
 &= \frac{8 - 8\alpha + \alpha}{8} \\
 &= \frac{8 - 7\alpha}{8} = \frac{8 - 7 \times 0.5}{8} = \frac{4.5}{8} = 0.5625
 \end{aligned}$$

Alternate method

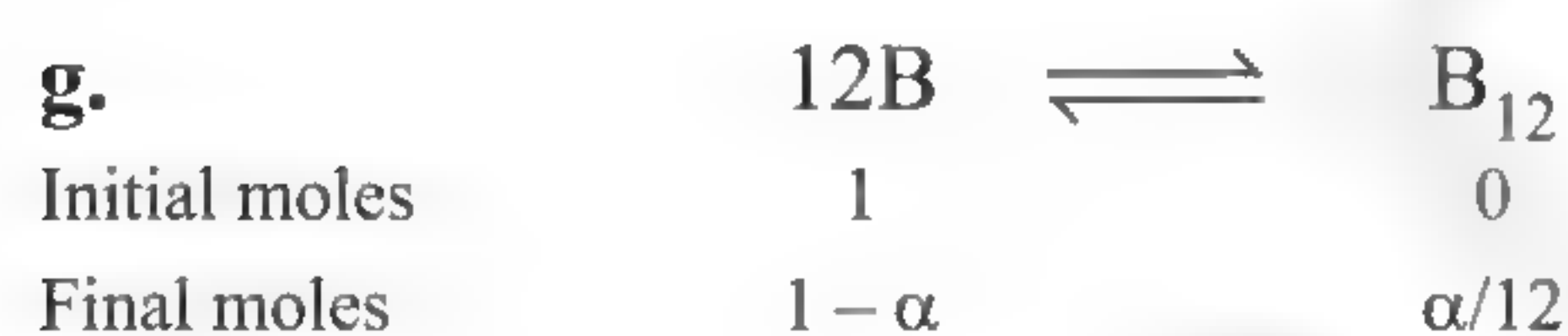
$$\begin{aligned}
 i &= (\text{Number of ions} \times \alpha) + (1 - \alpha) \\
 &= \left(\frac{1}{8} \times 0.5\right) + (1 - 0.5) = \frac{0.5}{8} + 0.5 \\
 \therefore i &= \frac{4.5}{8} = 0.5625
 \end{aligned}$$

(d, e, f)

$$\begin{aligned}
 i &= \frac{1 - \alpha + \frac{\alpha}{4}}{1} \\
 &= \frac{4 - 4\alpha + \alpha}{4} \\
 &= \frac{4 - 3\alpha}{4} = \frac{4 - 3 \times 0.5}{4} = \frac{2.5}{4} = 0.625
 \end{aligned}$$

Alternate method

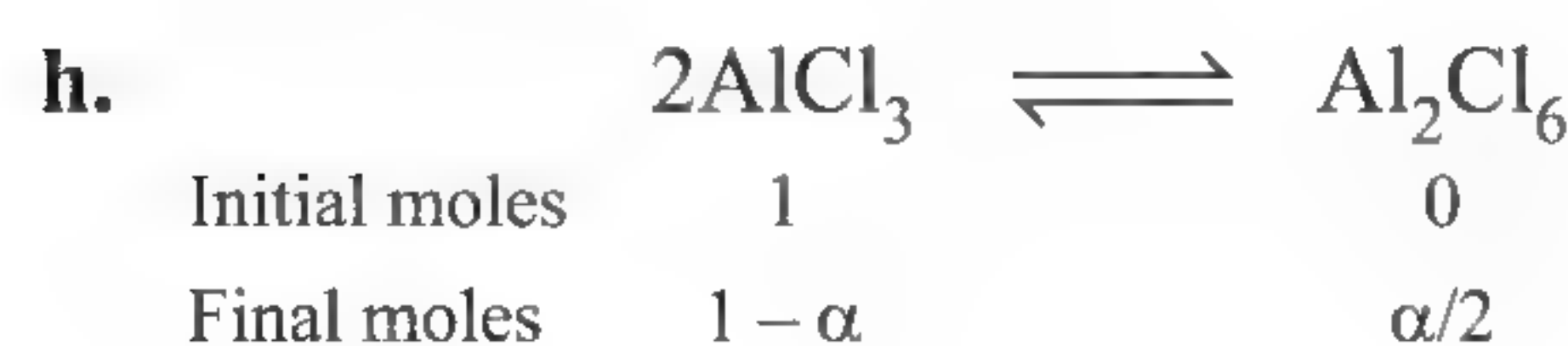
$$\begin{aligned}
 i &= (\text{Number of ions} \times \alpha) + (1 - \alpha) \\
 &= \left(\frac{1}{4} \times 0.5\right) + (1 - 0.5) \\
 &= \frac{0.5}{4} + 0.5 = \frac{2.5}{4} = 0.625
 \end{aligned}$$



$$\begin{aligned}
 i &= \frac{1 - \alpha + \frac{\alpha}{12}}{1} \\
 &= \frac{12 - 12\alpha + \alpha}{12} \\
 &= \frac{12 - 11\alpha}{12} = \frac{12 - 11 \times 0.5}{12} = \frac{6.5}{12} = 0.54
 \end{aligned}$$

Alternate method

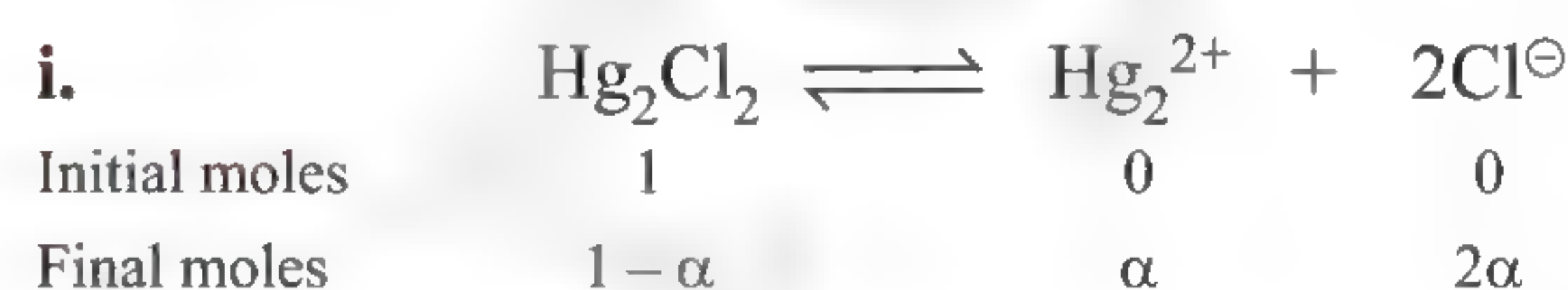
$$\begin{aligned}
 i &= (\text{Number of ions} \times \alpha) + (1 - \alpha) \\
 &= \left(\frac{1}{12} \times 0.5\right) + (1 - 0.5) \\
 &= \frac{0.5}{12} + 0.5 = \frac{6.5}{12} = 0.54
 \end{aligned}$$



$$i = \frac{1 - \alpha + \frac{\alpha}{2}}{1} = 1 - \frac{\alpha}{2} = 1 - \frac{0.5}{2} = \frac{1.5}{2} = 0.75$$

Alternate method

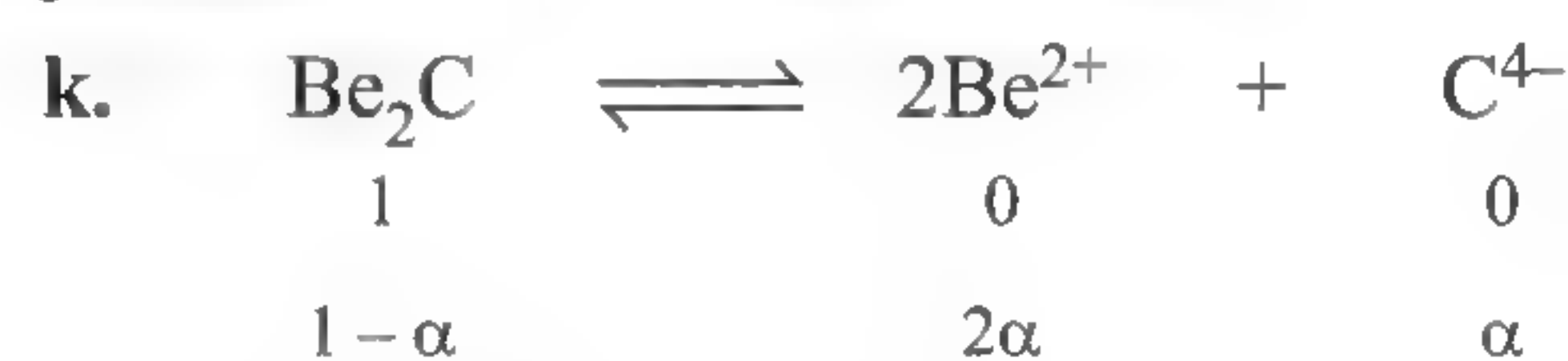
$$\begin{aligned}
 i &= (\text{Number of ions} \times \alpha) + (1 - \alpha) \\
 &= \left(\frac{1}{2} \times 0.5\right) + (1 - 0.5) \\
 &= \frac{0.5}{2} + 0.5 = \frac{1.5}{2} = 0.75
 \end{aligned}$$



$$i = \frac{1 - \alpha + \alpha + 2\alpha}{1} = 1 + 2\alpha = 1 + 2 \times 0.5 = 2$$

Alternate method

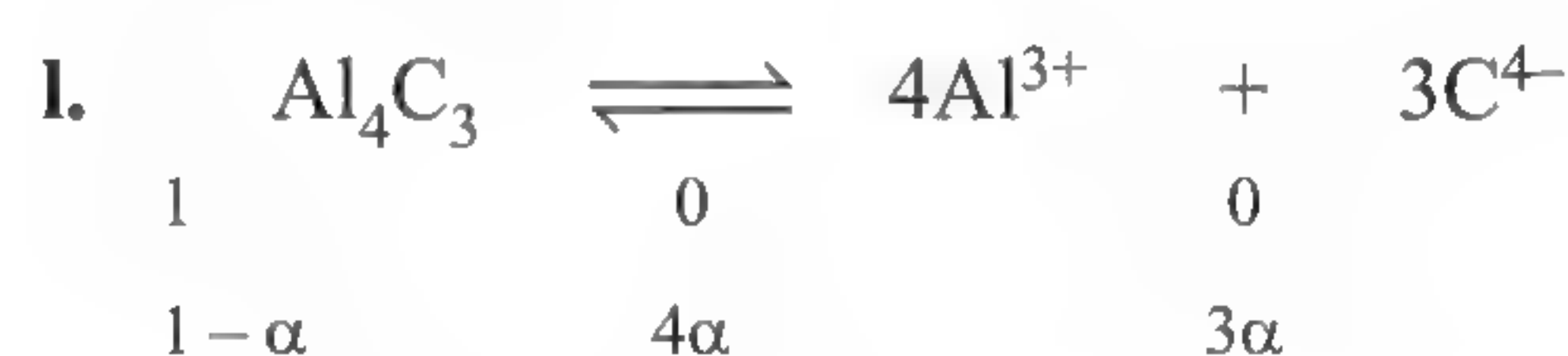
$$\begin{aligned}
 i &= (\text{Number of ions} \times \alpha) + (1 - \alpha) \\
 &= (3 \times 0.5) + (1 - 0.5) \\
 &= 1.5 + 0.5 = 2
 \end{aligned}$$

j. Since $i = 1$, it does not ionize.

$$i = \frac{1 - \alpha + 2\alpha + \alpha}{1} = 1 + 2\alpha = 1 + 2 \times 0.5 = 2$$

Alternate method

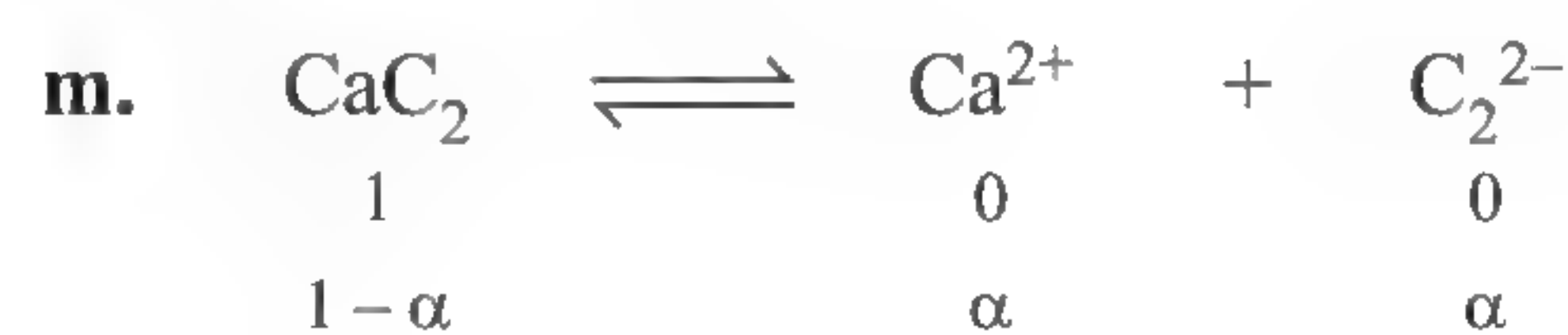
$$\begin{aligned}
 i &= (\text{Number of ions} \times \alpha) + (1 - \alpha) \\
 &= (3 \times 0.5) + (1 - 0.5) \\
 &= 1.5 + 0.5 = 2
 \end{aligned}$$



$$i = \frac{1 - \alpha + 4\alpha + 3\alpha}{1} = 1 + 6\alpha = 1 + 6 \times 0.5 = 4$$

Alternate method

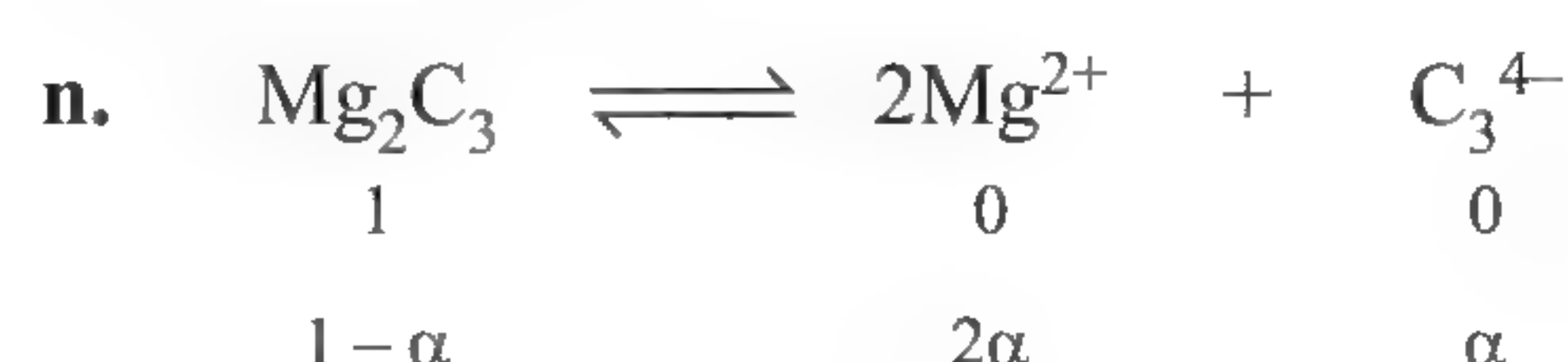
$$\begin{aligned}
 i &= (\text{Number of ions} \times \alpha) + (1 - \alpha) \\
 &= (7 \times 0.5) + (1 - 0.5) \\
 &= 3.5 + 0.5 = 4
 \end{aligned}$$



$$i = \frac{1 - \alpha + \alpha + \alpha}{1} = 1 + \alpha = 1 + 0.5 = 1.5$$

Alternate method

$$\begin{aligned}
 i &= (\text{Number of ions} \times \alpha) + (1 - \alpha) \\
 &= (2 \times 0.5) + (1 - 0.5) \\
 &= 1.0 + 0.5 = 1.5
 \end{aligned}$$



$$i = \frac{1 - \alpha + 2\alpha + \alpha}{1} = 1 + 2\alpha = 1 + 2 \times 0.5 = 2$$

Alternate method

$$\begin{aligned} i &= (\text{Number of ions} \times \alpha) + (1 - \alpha) \\ &= (3 \times 0.5) + (1 - 0.5) \\ &= 1.5 + 0.5 = 2 \end{aligned}$$

CONCEPT APPLICATION EXERCISE 2.3

1. A certain solution of 1 molal benzoic acid in benzene has a freezing point of 3.1°C and a normal boiling point of 82.6°C . The freezing point of benzene is 5.5°C and its boiling point is 80.1°C . K_f of benzene = 5.12 K/m and $K_b = 2.53 \text{ K/m}$. Analyse the state of the solute (benzoic acid) at two temperatures and comment.
2. A solution is prepared by dissolving 1.5 g of a monoacidic base into 1.5 kg of water at 300 K which showed a depression in freezing point by 0.165°C . When 0.496 g of the same base is titrated, after dissolution, requires 40 mL of semimolar H_2SO_4 solution. If K_f of water is $1.86 \text{ K kg mol}^{-1}$, then select correct statement(s) out of the following (assuming molarity = molality):
 - a. The pH of the solution of weak base is 12.9.
 - b. Ionization constant of the base is 8×10^{-3} .
 - c. The osmotic pressure of the aqueous solution of base is 21.67 atm.
 - d. The base is 10% ionized in aqueous solution.
3. Tritium T^3 (an isotope of H) combines with fluorine to form weak acid TF, which gets ionized to give T^+ . A freshly prepared aqueous solution of TF has pT (equivalent of pH) of 1.5 and freezes at -0.372°C . If 600 mL of freshly prepared solution were allowed to start for 24.8 years, calculate the ionization constant of TF. (Given K_f for $\text{H}_2\text{O} = 1.86$)
4. A dilute solution contains m mol of solute A in 1 kg of a solvent with molal elevation constant K_b , the solute dimerizes in solution as $2\text{A} \rightleftharpoons \text{A}_2$. Show that equilibrium constant for this dimer formation is $K = \frac{K_b(K_b m - \Delta T_b)}{(2\Delta T_b - K_b m)^2}$, where ΔT_b is the elevation in boiling point for the given.
5. Two liquids A and B form an ideal solution. If the mole fraction of A is χ at room temperature, the vapour pressure of solution is 85 mm. On the other hand if the mole fraction of B is χ at room temperature, the vapour pressure of solution is 95 mm. If $P_A^\circ/P_B^\circ = 1.25$, and the pressure over the mixture composed of 2 mol of A and 3 mol of B

at room temperature is reduced, at what pressure will the first trace of vapour form and what will be its composition?

6. The composition of vapour over a binary ideal solution is determined by the composition of the liquid. If X_A and Y_A are the mole fractions of A in the liquid and vapour, respectively find the value of X_A for which $Y_A - X_A$ has a minimum. What is the value of pressure at this composition?
7. Dry air was successively passed through a solution of 5 g solute in 80 g water and then through pure water. The loss in the weight of solution was 2.5 g and that of pure water was 0.04 g. What is the molecular weight of solute?
8. Two beaker A and B present in a closed vessel. Beaker A contains 152.4 g aqueous solution of urea, containing 12 g of urea. Beaker B contains 196.2 g glucose solution, containing 18 g of glucose. Both solutions are allowed to attain the equilibrium. Determine mass % of glucose in its solution at equilibrium:
9. At 48°C , the vapour pressure of pure CS_2 is 850 torr. A solution of 2.0 g of sulphur in 100 g of CS_2 has a vapour pressure 844.9 torr. Determine the atomicity of sulphur molecule:
10. An ideal solution contains two volatile liquids A ($P^\circ = 100$ torr) and B ($P^\circ = 200$ torr). If mixture contain 1 mole of A and 4 mole of B then total vapour pressure of the distillate is:
11. The vapour pressure of two pure liquids A and B, that form an ideal solution are 100 and 900 torr respectively at temperature T . This liquid solution of A and B is composed of 1 mole of A and 1 mole of B. What will be the pressure, when 1 mole of mixture has been vaporized?
12. An industrial waste water is found to contain 8.2% Na_3PO_4 and 12% MgSO_4 by mass in solution. If % ionisation of Na_3PO_4 and MgSO_4 are 50 and 60 respectively then its normal boiling point is [$K_b(\text{H}_2\text{O}) = 0.50 \text{ K kg mol}^{-1}$]
13. Ratio of $\frac{\Delta T_b}{K_b}$ of 10 g AB_2 and 14 g A_2B per 100 g of solvent in their respective, solution (AB_2 and A_2B both are non-electrolytes) is 1 mol/kg in both cases. Hence, atomic wt of A and B are respectively:
14. If boiling point of an aqueous solution is 100.1°C , what is its freezing point? Given, enthalpy of fusion and vaporisation of water are 80 cal g^{-1} and 540 cal g^{-1} respectively.
15. 0.1 M KI and 0.2 M AgNO_3 are mixed in 3 : 1 volume ratio. The depression of freezing point of the resulting solution will be [$K_f(\text{H}_2\text{O}) = 1.86 \text{ K kg mol}^{-1}$]:

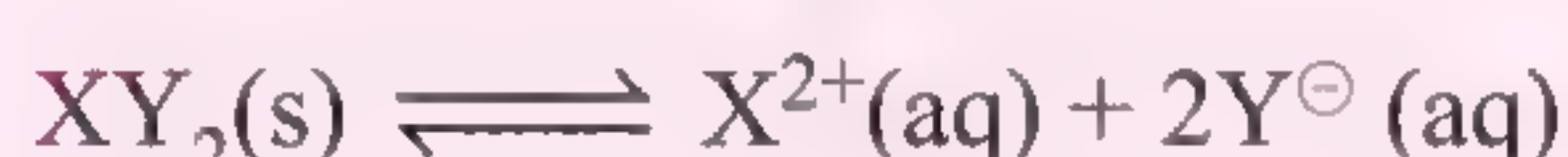
16. The total pressure of a 4 mole % solution of NH_3 in water at 293 K is 50.0 torr. The vapour pressure of pure water is 17.0 torr at this temperature, Applying Henry's and Raoult's laws, calculate the total vapour pressure for a 5 mole % solution.

17. The total pressure of two pure liquids A and B which form an ideal solution are 500 and 800 torr respectively at 300 K. A liquid solution of A and B for which the mole fraction of A is 0.06 is contained in a cylinder closed by a piston on which the pressure can be varied. The solution is slowly vaporized at 300 K by decreasing the applied pressure.

The composition of vapour when first bubble formed is:

18. Refer to Q. 17 above. What is the composition of last droplet of liquid remaining in equilibrium with vapour?

19. The K_{sp} (25°C) of sparingly soluble salt $\text{XY}_2(\text{s})$ is $3.56 \times 10^{-5} (\text{mol L}^{-1})^3$ and at 30°C, the vapour pressure of its saturated solution in water is 31.78 mm of Hg. Calculate the enthalpy change of the reaction



Given: Vapour pressure of pure water = 31.82 mm of Hg

20. Phenol associates in benzene to certain extent to form a dimer. A solution containing 20×10^{-3} kg of phenol in

1.0 kg of benzene has its freezing point depressed by 0.69 K. Calculate the fraction of phenol that has dimerized. (K_f for benzene is $5.12 \text{ K kg mol}^{-1}$).

21. 3 g of urea and 9 g of another non-volatile electrolytic compound (XY_2) were dissolved in 1000 g of water. The degree of dissociation of XY_2 is 0.5. The solution has a vapour pressure of 328.515 mm. Find the vapour density of XY_2 . The vapour pressure of water is 330 mm.

ANSWERS

1. Benzoic acid neither associate or dissociate at high temp.

2. (a, b, c, d) 3. $k = 7.299 \times 10^{-3}$ 4. Factual

5. $P = 88 \text{ mm}$ 7. $MW = 70.31$

8. Wt% of glucose = 14.49 9. Atomicity of sulphur = 8

10. $P_{\text{Total}} = 188.88 \text{ torr}$ 11. $P = 300 \text{ torr}$

12. $T_b = 101.785^\circ\text{C}$ 13. $M_A = 60, M_B = 20$

14. $T_f = -0.361^\circ\text{C}$ 15. $\Delta T_f = 0.279 \text{ K}$

16. $P_{\text{Total}} = 58.25 \text{ torr}$ 17. $y_A = 0.48, y_B = 0.52$

18. $x_A = 0.70, x_B = 0.30$ 19. $\Delta H = 52.5 \text{ kJ mol}^{-1}$

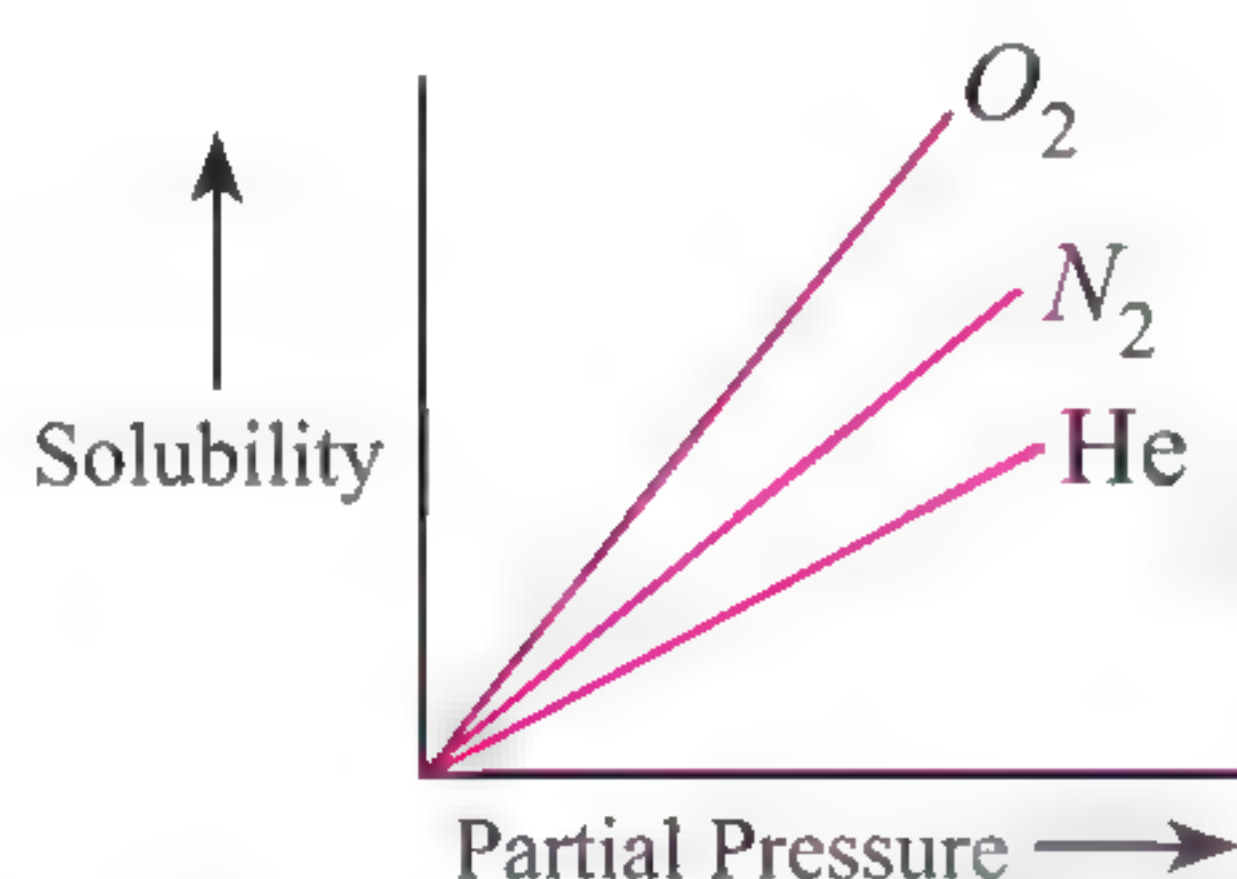
20. $\alpha = 0.733$ 21. V.D = 44.8

Exercises

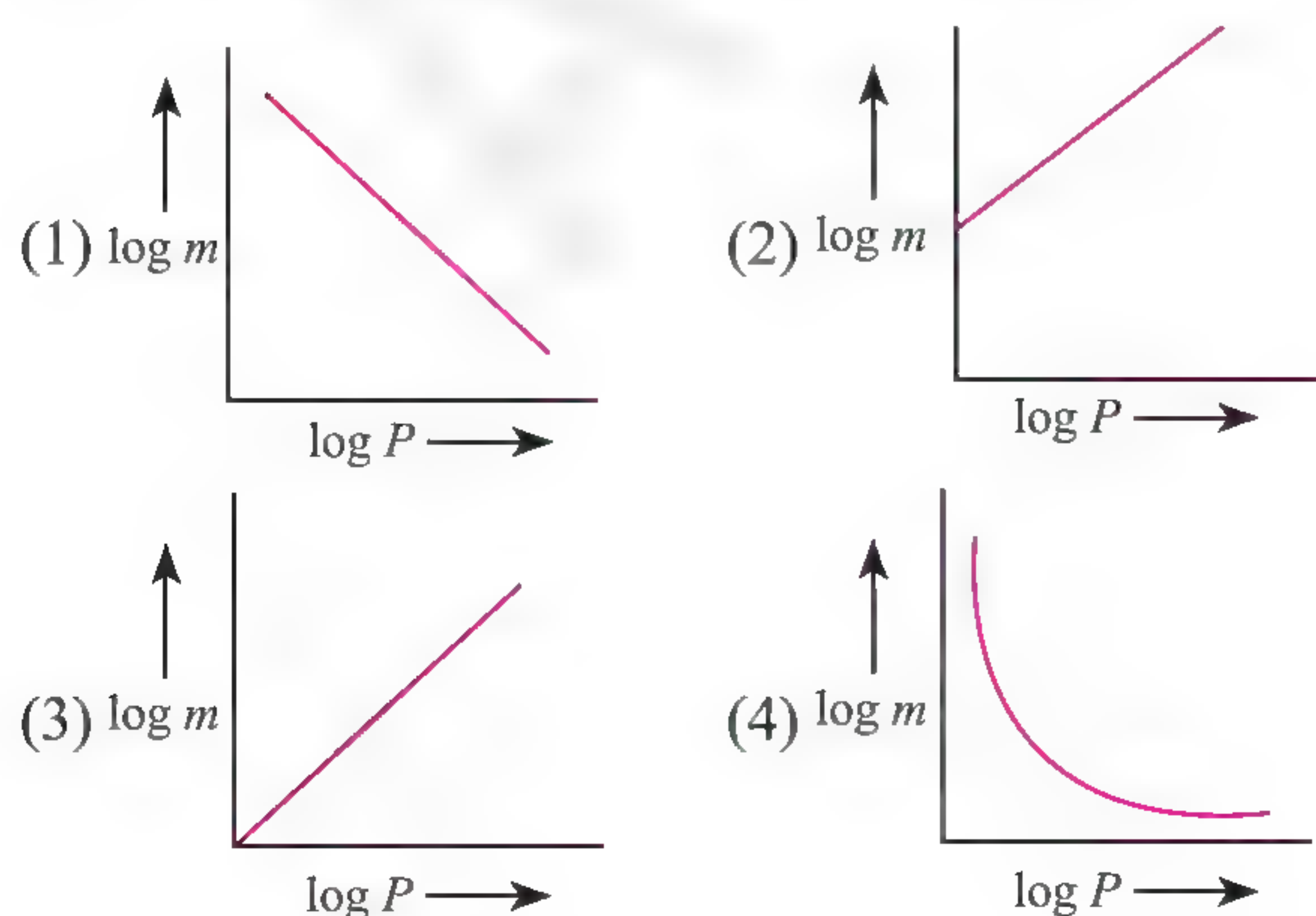
Single Correct Answer Type

Henry's Law

- At same temperature, oxygen is more soluble in water than hydrogen. Which of them will have a higher value of K_H ?
 (1) Oxygen (2) Hydrogen
 (3) Both have equal value (4) Can't predict
- Henry's law is valid only when:
 (1) Pressure is low
 (2) Temperature is low
 (3) The gas is not highly soluble
 (4) The gas neither reacts chemically with solvent nor dissociates or associates in the solvent.
- Air contains O_2 and N_2 in the ratio of 1 : 4. Calculate the ratio of solubilities in terms of mole fractions of N_2 and O_2 dissolved in water at atmospheric pressure and at room temperature at which Henry's constant for O_2 and N_2 are 3.30×10^7 and 6.60×10^7 torr respectively.
 (1) 1 : 2 (2) 2 : 1
 (3) 3 : 1 (4) 1 : 3
- Molar solubility of helium, nitrogen and oxygen are plotted against partial pressure of the gas at constant temperature. Henry's law constant for these gases will lie in following sequence?



- (1) $O_2 > N_2 > He$ (2) $O_2 < N_2 < He$
 (3) $O_2 = N_2 = He$ (4) $O_2 > N_2 < He$
- According to William Henry's the solubility of a gas in liquid depends on the pressure of the gas. If 'm' is the molality of the gas and 'P' is its pressure, then which of the following plot is in accordance with the law?



- Which of the following units is useful in relating concentration of solution with its vapour pressure?
 (1) Mole fraction (2) Parts per million
 (3) Mass percentage (4) Molality
- A sample of water is contaminated with 30 ppm of arsenic (As). The molality of As in water is (A_w of As = 75.0 g)
 (1) 2×10^{-2} (2) 4×10^{-2}
 (3) 2×10^{-3} (4) 4×10^{-3}
- K_H (Henry's law constant) for CO_2 in water at $25^\circ C$ is $3.0 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}$. What is the concentration of CO_2 in soft drink that is bottled with a partial pressure of CO_2 of 5 atm. over the liquid at $25^\circ C$
 (1) 0.15 M (2) 0.015 M
 (3) 0.30 M (4) 0.03 M

Raoult's Law, Ideal and Non-Ideal Solution, Azeotrope

- 0.2 mole of liquid A is dissolved in 4.0 mole of H_2O . Total pressure of solution is 0.210 bar at $37^\circ C$. The vapour pressure of pure liquid (vapour pressure of water at $37^\circ C = 0.198$ bar) in bar is
 (1) 0.448 (2) 44.8
 (3) 0.224 (4) 2.24
- Two liquids A and B form an ideal solution. The vapour pressure of pure A and pure B are 66 mm Hg and 88 mm Hg, respectively. Calculate the composition of vapour A in the solution which is equilibrium and whose molar volume is 36%.
 (1) 0.43 (2) 0.70
 (3) 0.30 (4) 0.50
- At $27^\circ C$, the vapour pressure of an ideal solution containing 1 mole of A and 1 mole of B is 500 mm of Hg. At the same temperature, if 2 mol of B is added to this solution the vapour pressure of solution increases by 50 mm of Hg. The vapour pressure of A and B in their pure states is respectively,
 (1) 600 mm, 400 mm (2) 400 mm, 600 mm
 (3) 300 mm, 700 mm (4) 200 mm, 800 mm
- Mixture of volatile components A and B has total vapour pressure (in torr) : $P_{\text{total}} = 254 - 119\chi_A$ where χ_A is the mole fraction of A in mixture. Hence p_A° and p_B° are (in torr):
 (1) 254, 119 (2) 119, 254
 (3) 135, 254 (4) 154, 119
- Negative deviations from Raoult's law are exhibited by binary mixtures
 (1) in which the molecules tend to attract each other and hence their escape into the vapour phase is retarded.
 (2) in which the molecules tend to repel each other and hence their escape into the vapour phase is retarded.
 (3) in which the molecules tend to attract each other and hence their escape into the vapour phase is speeded up.

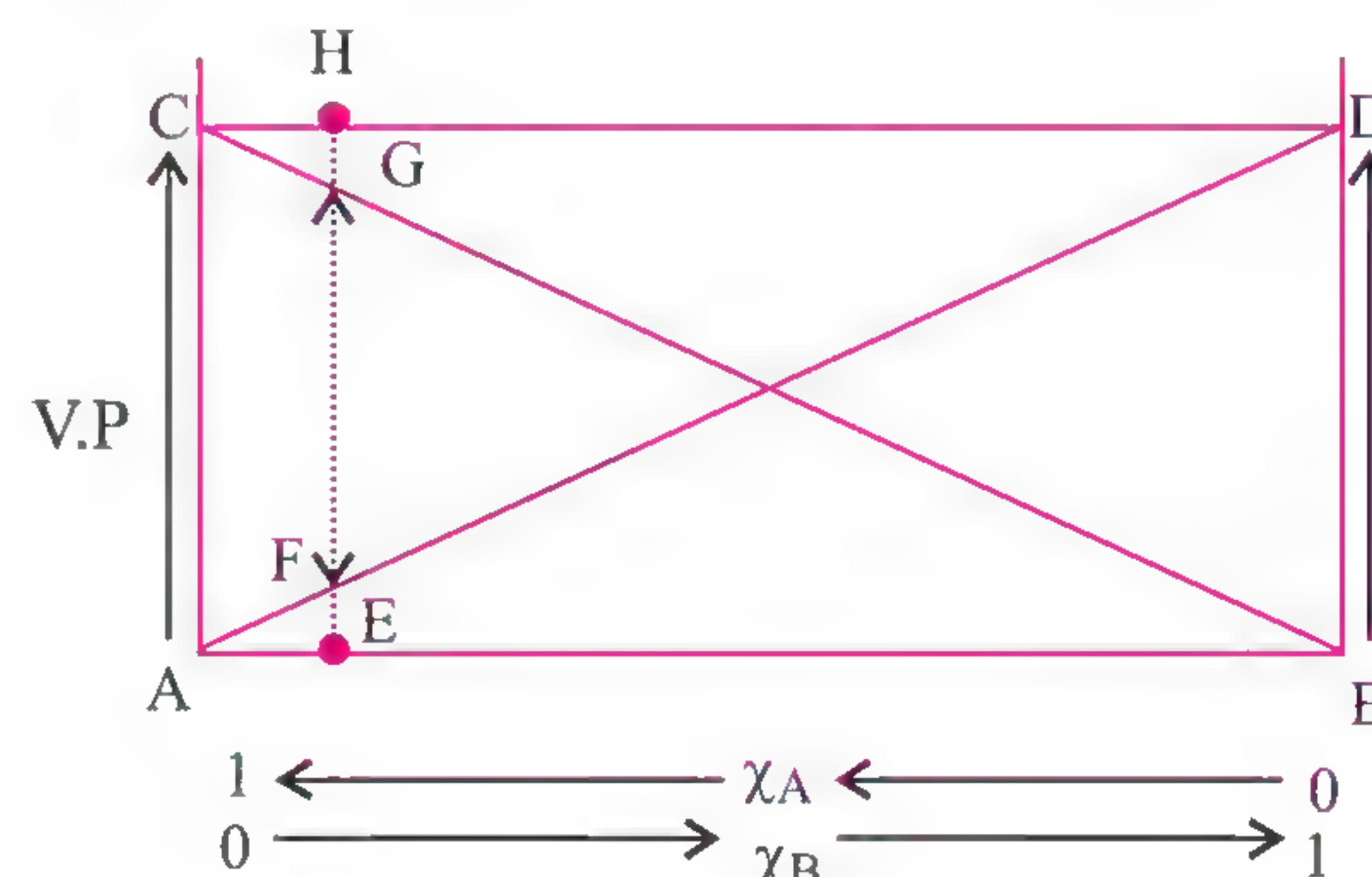
- (4) in which the molecules tend to repel each other and hence their escape into the vapour phase is speeded up.
14. Mole fraction of component A in vapour phase is χ_1 and mole fraction of component A in liquid mixture is χ_2 (p_A° = vapour pressure of pure A), then the total vapour pressure of the liquid mixture is
- (1) $\frac{p_A^\circ \chi_2}{\chi_1}$ (2) $\frac{p_A^\circ \chi_1}{\chi_2}$
 (3) $\frac{p_B^\circ \chi_1}{\chi_2}$ (4) $\frac{p_B^\circ \chi_2}{\chi_1}$
15. At 25°C, the vapour pressure of pure methyl alcohol is 92.0 torr. Mol fraction of CH₃OH in a solution in which vapour pressure of CH₃OH is 23.0 torr at 25°C, is:
- (1) 0.25 (2) 0.75
 (3) 0.50 (4) 0.66
16. The vapour pressure of pure benzene C₆H₆ at 50°C is 268 torr. How many moles of non-volatile solute per mole of benzene are required to prepare a solution of benzene having a vapour pressure of 167 torr at 50°C?
- (1) 0.377 (2) 0.605
 (3) 0.623 (4) 0.395
17. The vapour pressure of pure liquid solvent A is 0.80 atm. When a non-volatile substance B is added to the solvent, its vapour pressure drops to 0.60 atm; the mole fraction of component B in the solution is
- (1) 0 (2) 0.25
 (3) 2.0 (4) 3.0
18. The vapour pressure of a pure liquid A is 40 mm Hg at 310 K. The vapour pressure of this liquid in a solution with liquid B is 32 mm Hg. The mole fraction of A in the solution, if it obeys Raoult's law, is:
- (1) 0.8 (2) 0.5
 (3) 0.2 (4) 0.4
19. The boiling point of an azeotropic mixture of water and ethyl alcohol is less than that of the theoretical value of water and alcohol mixture. Hence the mixture shows
- (1) The solution is highly saturated.
 (2) Positive deviation from Raoult's law.
 (3) Negative deviation from Raoult's law.
 (4) Nothing can be said.
20. Solution distilled without change in composition at a temperature is called
- (1) Amorphous (2) Azeotropic mixture
 (3) Ideal solution (4) Super saturated solution
21. Azeotropic mixtures are
- (1) Constant boiling point mixture without changing the composition.
 (2) Those which boil at different temperatures.
 (3) Mixtures of two solids.
 (4) None of the above
22. On mixing 10 mL of acetone with 40 mL of chloroform, the total volume of the solution is
- (1) <50 mL (2) >50 mL
 (3) =50 mL (4) Cannot be predicted
23. Which of the following substances will lose its solubility with increase in temperature?
- (1) NaOH (2) Na₂CO₃ (3) Na₂SO₄ (4) All
24. On mixing 10 mL of carbon tetrachloride with 10 mL of benzene, the total volume of the solution is
- (1) >20 mL (2) <20 mL
 (3) =20 mL (4) Cannot be predicted
25. If Raoult's law is obeyed, the vapour pressure of the solvent in a solution is directly proportional to
- (1) The mole fraction of the solvent.
 (2) The mole fraction of the solute.
 (3) The mole fraction of the solvent and solute.
 (4) The volume of the solution.
26. Each pair forms ideal solution except
- (1) C₂H₅Br and C₂H₅I
 (2) C₆H₅Cl and C₆H₅Br
 (3) C₆H₆ and C₆H₅·CH₃
 (4) C₂H₅I and C₂H₅OH
27. An aqueous solution of methanol in water has vapour pressure
- (1) Equal to that of water
 (2) Equal to that of methanol
 (3) More than that of water
 (4) Less than that of water
28. Which condition is not satisfied by an ideal solution?
- (1) $\Delta_{\text{mix}}H = 0$
 (2) $\Delta_{\text{mix}}V = 0$
 (3) $\Delta_{\text{mix}}S = 0$
 (4) Obedience of Raoult's law
29. A mixture of benzene and toluene forms
- (1) An ideal solution (2) Non-ideal solution
 (3) Suspension (4) Emulsion
30. A pressure cooker reduces cooking time because
- (1) Heat is more evenly distributed
 (2) Boiling point of water inside the cooker is increased
 (3) The high pressure tenderizes the food
 (4) All of these
31. If P° and P_s are vapour pressures of solvent and its solution, respectively, χ_1 and χ_2 are mole fractions of solvent and solute, respectively, then
- (1) $P_s = P^\circ/\chi_2$
 (2) $P^\circ - P_s = P^\circ\chi_2$
 (3) $P_s = P^\circ\chi_2$
 (4) $\frac{P^\circ - P_s}{P_s} = \frac{\chi_1}{\chi_1 + \chi_2}$
32. Dry air was passed successively through a solution of 5 g of a solute in 180 g of water and then through pure water.

The loss in the weight of solution was 2.50 g and that of pure solvent 0.04 g. The molecular weight of the solute is

- (1) 31.25 (2) 3.125 (3) 312.5 (4) None
33. At 40°C, the vapour pressures of pure liquids, benzene, and toluene, are 160 mm Hg and 60 mm Hg, respectively. At the same temperature, the vapour pressure of an equimolar solution of the two liquids, assuming the ideal solution, should be
(1) 140 mm Hg (2) 110 mm Hg
(3) 220 mm Hg (4) 100 mm Hg
34. An azeotropic mixture of HCl and water has
(1) 84% of HCl (2) 22.2% HCl
(3) 63% of HCl (4) 20.2% HCl
35. An ideal solution was obtained by mixing methanol and ethanol. If the partial vapour pressure of methanol and ethanol are 2.619 kPa and 4.556 kPa, respectively, the composition of vapour (in terms of mole fraction) will be
(1) 0.635 MeOH, 0.365 EtOH
(2) 0.365 MeOH, 0.635 EtOH
(3) 0.574 MeOH, 0.326 EtOH
(4) 0.173 MeOH, 0.827 EtOH
36. The vapour pressure of a solvent decreased by 10 mm of Hg when a non-volatile solute was added to the solvent. The mole fraction of solute in solution is 0.2, what would be the mole fraction of solvent if the decrease in vapour pressure is 20 mm of Hg.
(1) 0.8 (2) 0.6 (3) 0.4 (4) 0.2
37. The mole fraction of toluene in the vapour phase which is in equilibrium with a solution of benzene ($P_B^\circ = 120$ torr) and toluene ($P_T^\circ = 80$ torr) having 2.0 mol of each, is
(1) 0.50 (2) 0.25 (3) 0.60 (4) 0.40
38. The total vapour pressure of a mixture of 1 mol A ($P_A^\circ = 150$ torr) and 2 mol B ($P_B^\circ = 240$ torr) is 200 mm. In this case
(1) There is positive deviation from Raoult's law.
(2) There is negative deviation from Raoult's law.
(3) There is no deviation from Raoult's law.
(4) Molecular masses of A and B are also required.
39. The vapour pressure of pure benzene C_6H_6 at 50°C is 268 torr. How many moles of non-volatile solute per mole of benzene is required to prepare a solution of benzene having a vapour pressure of 167 torr at 50°C?
(1) 0.377 (2) 0.605 (3) 0.623 (4) 0.395
40. The most likely of the following mixtures to be an ideal solution is
(1) NaCl—H₂O (2) C₂H₅OH—C₆H₆
(3) C₆H₁₆(l)—H₂O (4) C₆H₅OH—H₂O
41. The mole fraction of component A in vapour phase is χ_1 and mole fraction of component A in liquid mixture is χ_2 (P_A° = vapour pressure of pure A; P_B° = vapour pressure of pure B). Then total vapour pressure of the liquid mixture is

$$(1) \frac{P_A^\circ \chi_2}{\chi_1} \quad (2) \frac{P_A^\circ \chi_1}{\chi_2} \quad (3) \frac{P_A^\circ \chi_1}{\chi_2} \quad (4) \frac{P_B^\circ \chi_2}{\chi_1}$$

42. The relative decrease in the vapour pressure of an aqueous solution containing 2 mol $[Cu(NH_3)_3Cl]Cl$ in 3 mol H₂O is 0.50. On reaction with AgNO₃, this solution will form
(1) 1 mol AgCl (2) 0.25 mol AgCl
(3) 2 mol AgCl (4) 0.40 mol AgCl
43. A mixture of volatile components A and B has total vapour pressure (in torr)
 $P = 254 - 119\chi_A$
where χ_A is the mole fraction of A in mixture. Hence, P_A° and P_B° are (in torr)
(1) 254, 119 (2) 119, 254 (3) 135, 254 (4) 154, 119
44. Based on the given diagram, which of the following statements regarding the solutions of two miscible volatile liquids are correct?
- Plots AD and BC show that Raoult's law is obeyed for the solution in which B is a solvent and A is the solute and as well as for that in which A is solvent and B is solute.
 - Plot CD shows that Dalton's law of partial pressures is observed by the binary solutions of components A and B.
 - EF + EG = EH; and AC and BD corresponds to the vapour pressures of the pure solvents A and B, respectively.



Select the correct answer using the codes given below:

Codes:

- (1) 1 and 2 (2) 2 and 3
(3) 1 and 3 (4) 1, 2, and 3
45. Which of the following graph represent the behavior of ideal binary liquid mixture ?
(1) Plot of $1/P_{\text{Total}}$ against x_A is linear
(2) Plot of $1/P_{\text{Total}}$ against x_B is linear
(3) Plot of P_{Total} against x_A is linear
(4) Plot of P_{Total} against x_B is linear
(Here x_A and x_B are the mole fraction of components A and B in vapour phase)
46. A maxima of minima obtained in the temperature, composition curve of a mixture of two liquids indicates :
(1) An azeotropic mixture

- (2) An eutectic formation
 (3) That the liquids are immiscible with one another
 (4) that the liquids are partially miscible at the maximum or minimum

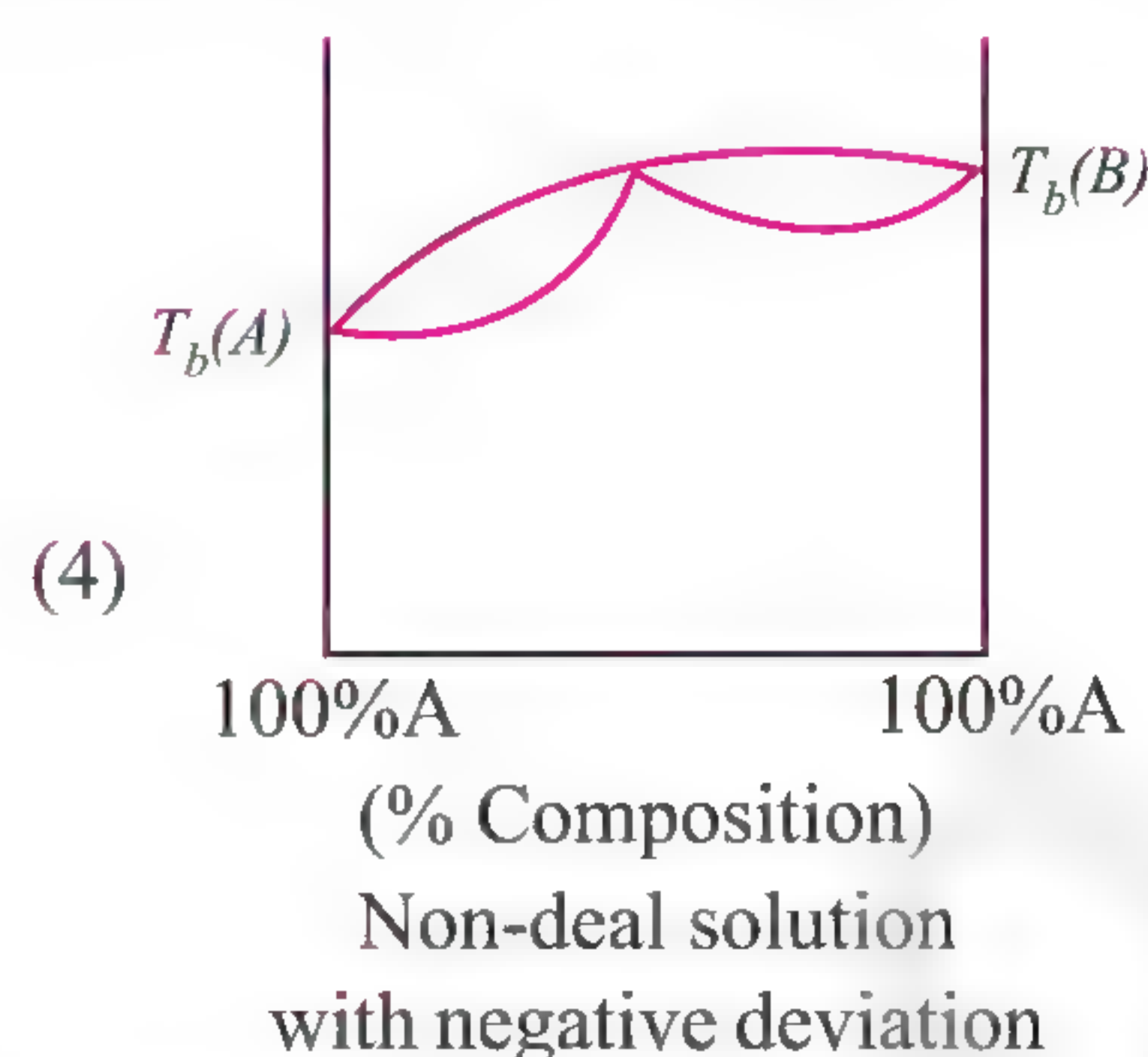
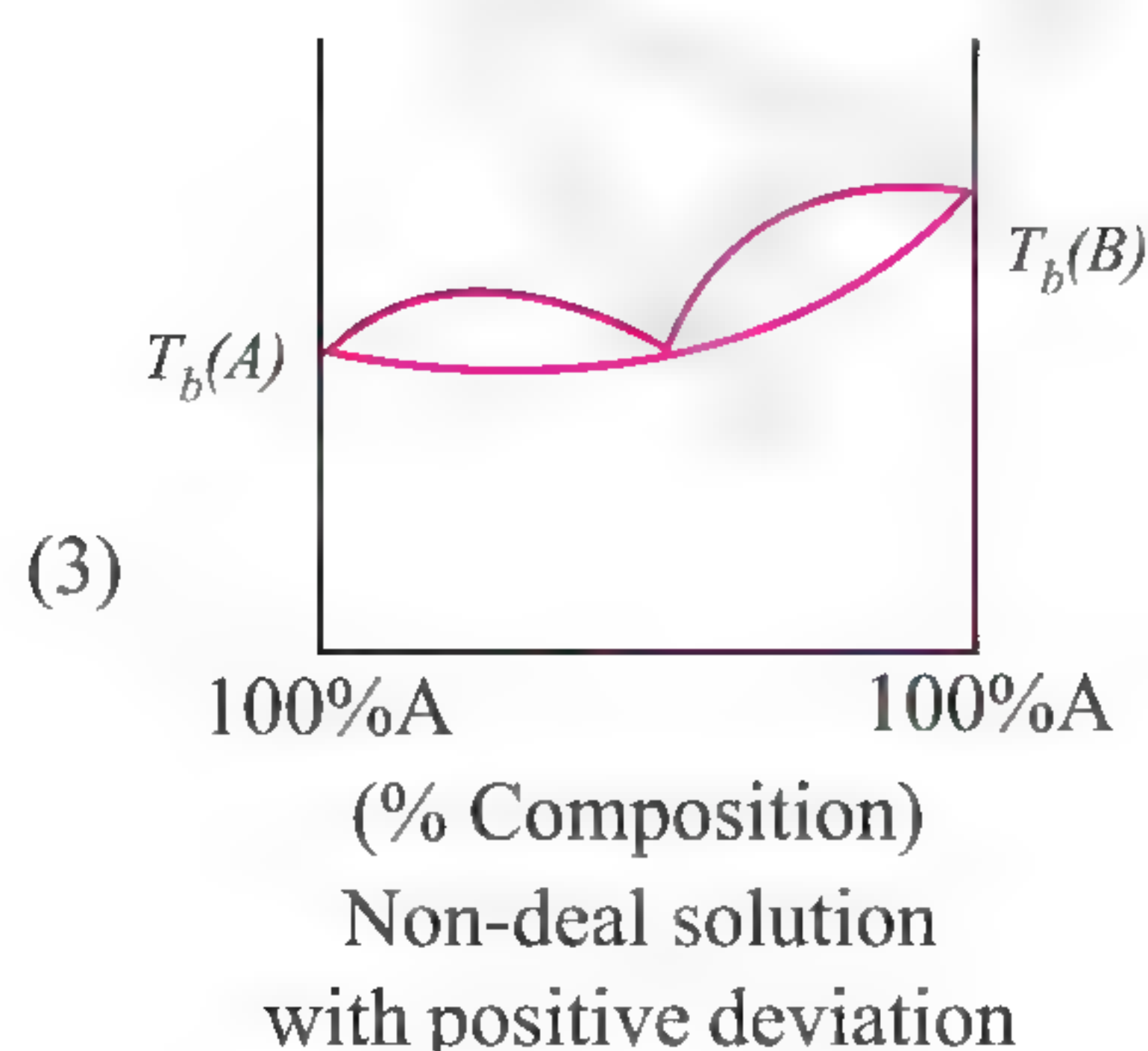
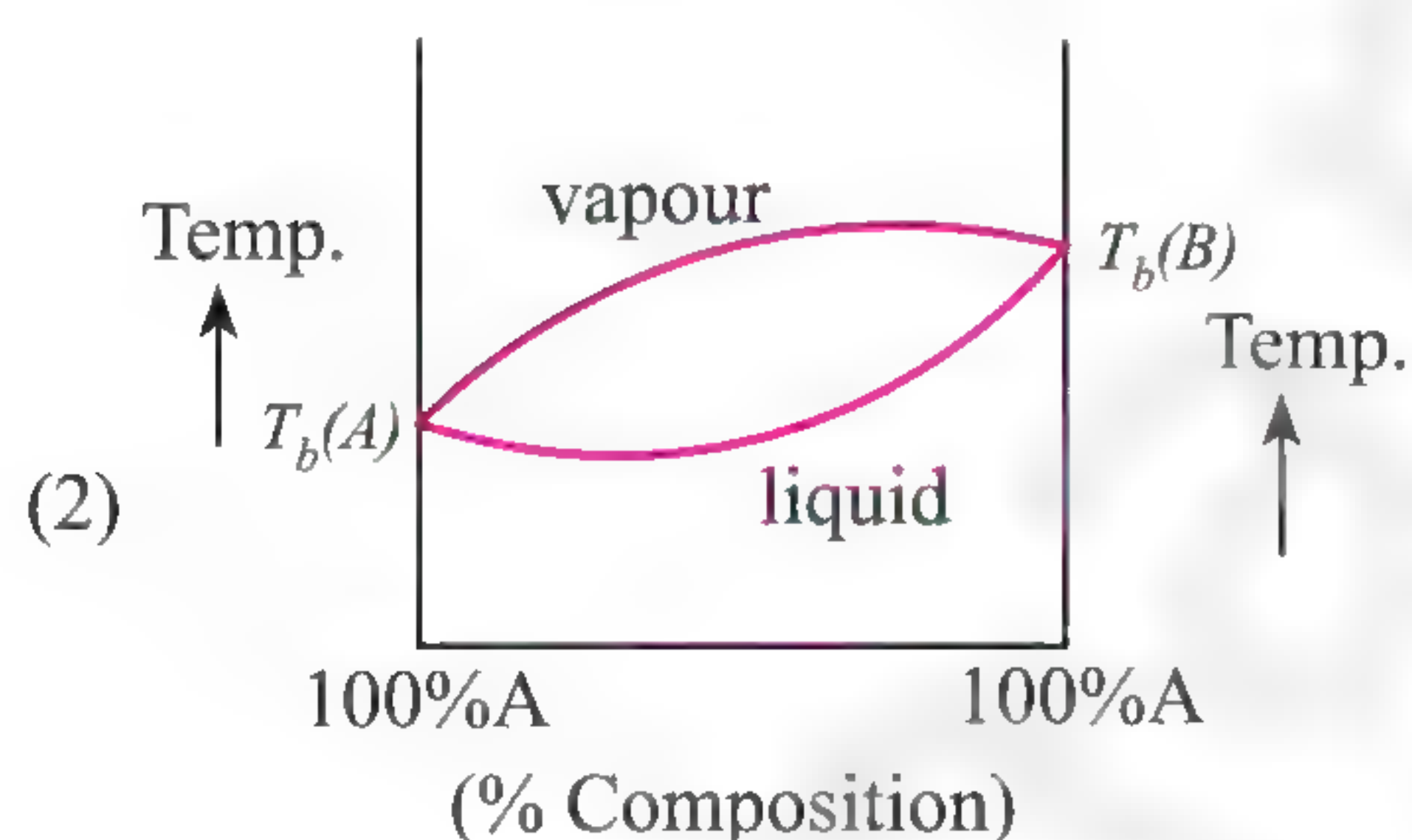
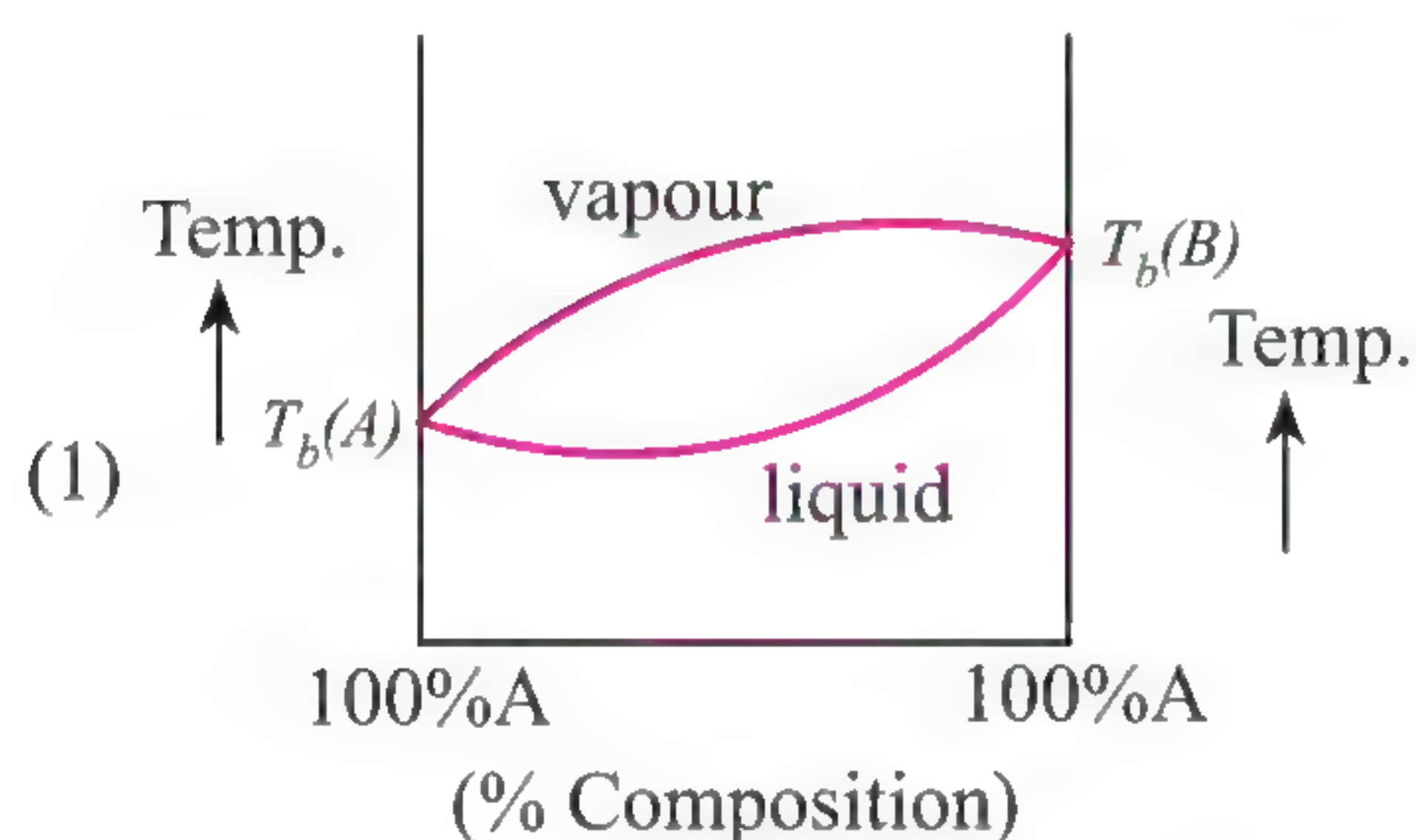
47. A solution has 1 : 4 mole ratio of pentane to hexane. The vapour pressure of pure hydrocarbons at 20°C are 440 mm Hg for pentane and 120 mm Hg for hexane. The mole fraction of pentane in vapour phase would be:

- (1) 0.786
 (2) 0.549
 (3) 0.478
 (4) 0.200

48. The lubricating action of an oil is more if it possess:

- (1) High vapour pressure
 (2) Low vapour pressure
 (3) High surface tension
 (4) High density

49. When a plot of boiling point versus composition is plotted, then type of graph than can be obtained is:



50. An ideal solution has two components A and B. If A is more volatile than B and also $P_A^0 > P_B^0$, then the correct relation between mole fraction of A in liquid (X) and vapour (Y) phase is :

- (1) $X_A = Y_A$ (2) $X_A > Y_A$
 (3) $X_A < Y_A$ (4) Can't be predicted

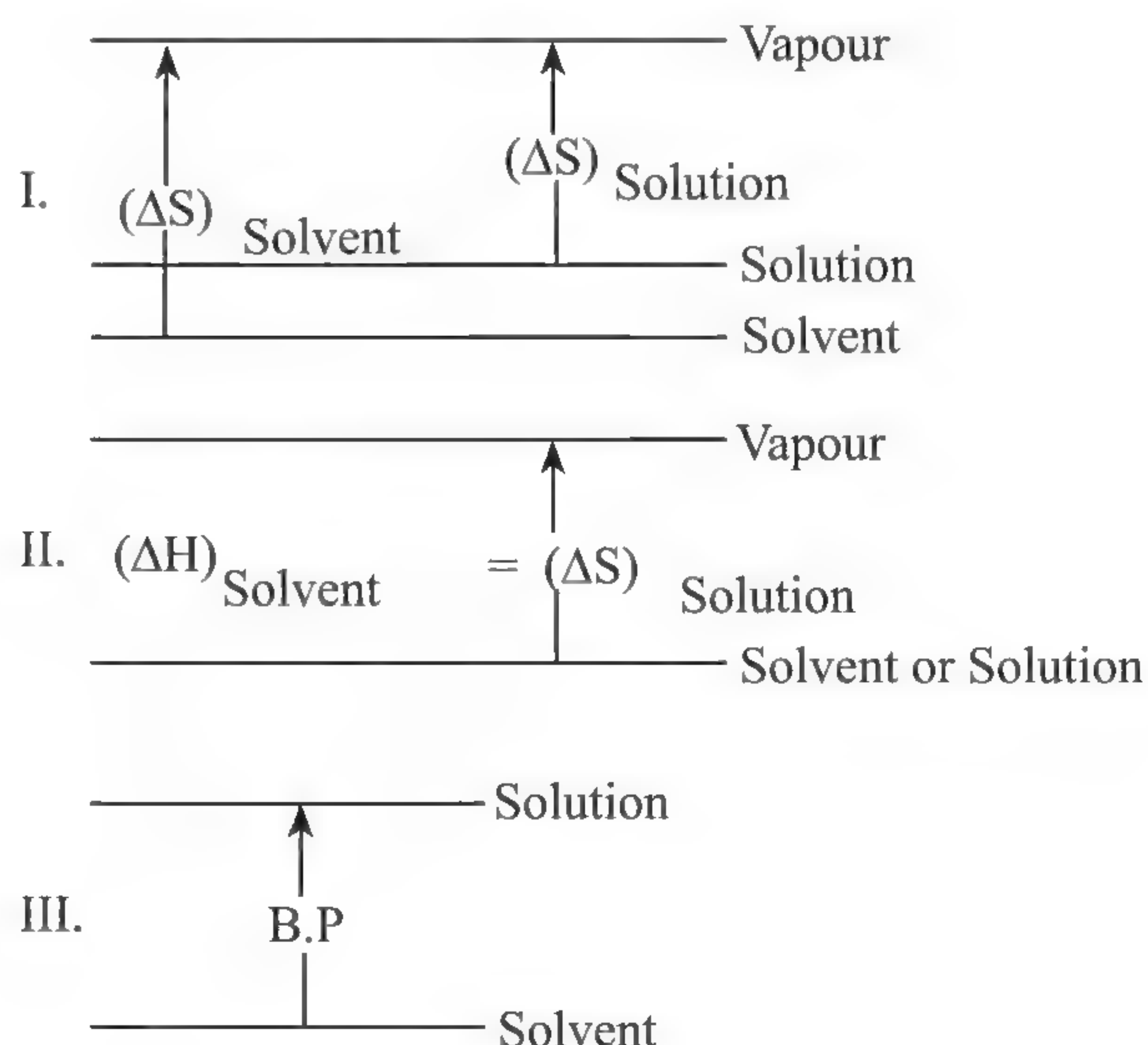
51. The normal boiling point of water is 373 K, Vapour pressure of water at temperature T is 19 mm Hg. If enthalpy of vaporisation is 40.67 kJ/mol, then temperature T would be (Use : $\log 2 = 0.3$, $R : 8.3 \text{ JK}^{-1} \text{ mol}^{-1}$):

- (1) 250 K (2) 291.4 K
 (3) 230 K (4) 290 K

52. Two liquids A and B have P_A^0 and P_B^0 in the ratio of 1 : 3 and the ratio of number of moles A and B in liquid phase are 1 : 3. Then mole fraction of 'A' in vapour phase in equilibrium with the solution is equal to"

- (1) 0.1 (2) 0.2
 (3) 0.5 (4) 1.0

53. Which represents correct difference when non-volatile solute is present in an ideal solution?

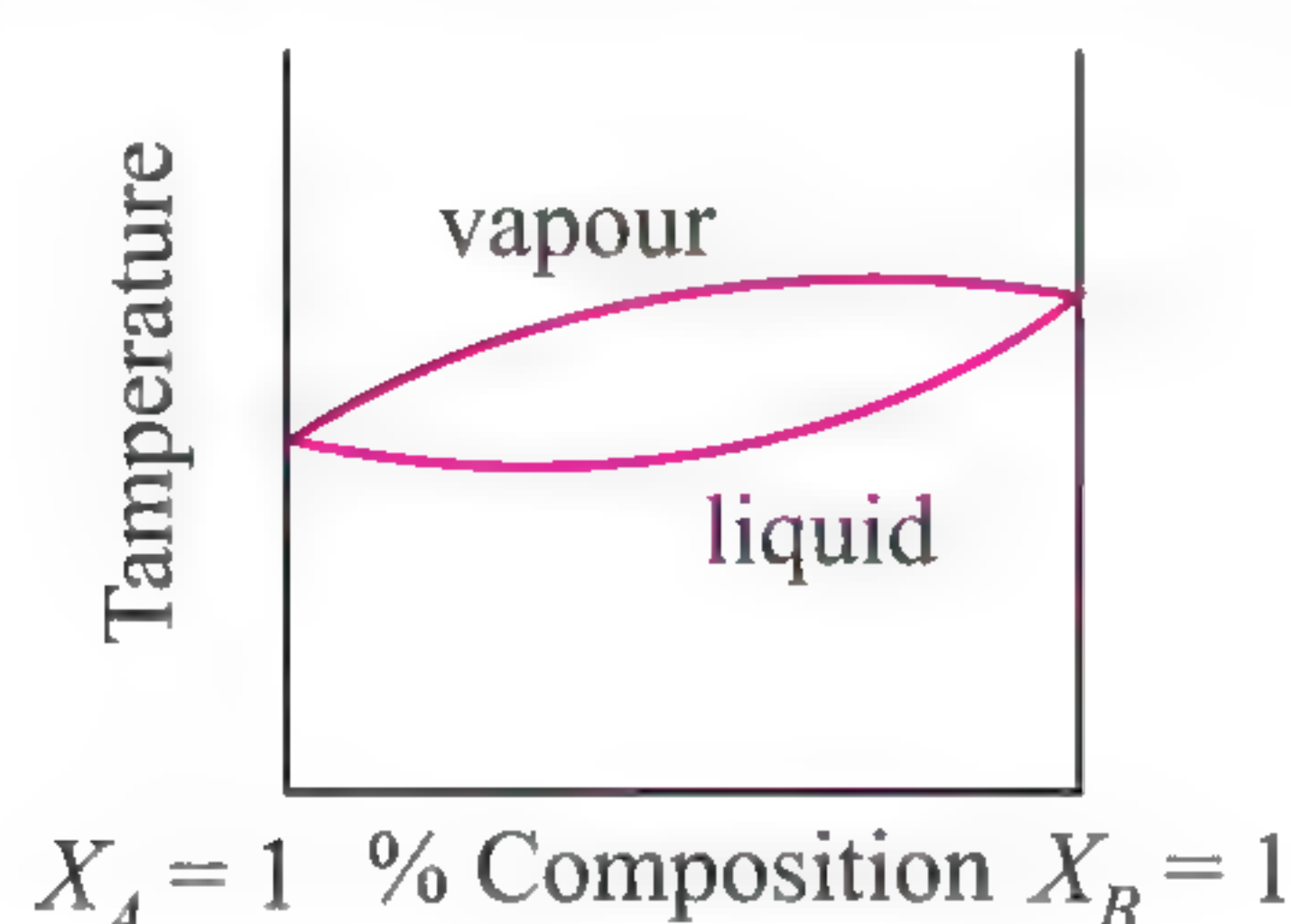


- (1) I, II, III (2) I, III
 (3) II, III (4) I, II

54. Select correct statement?

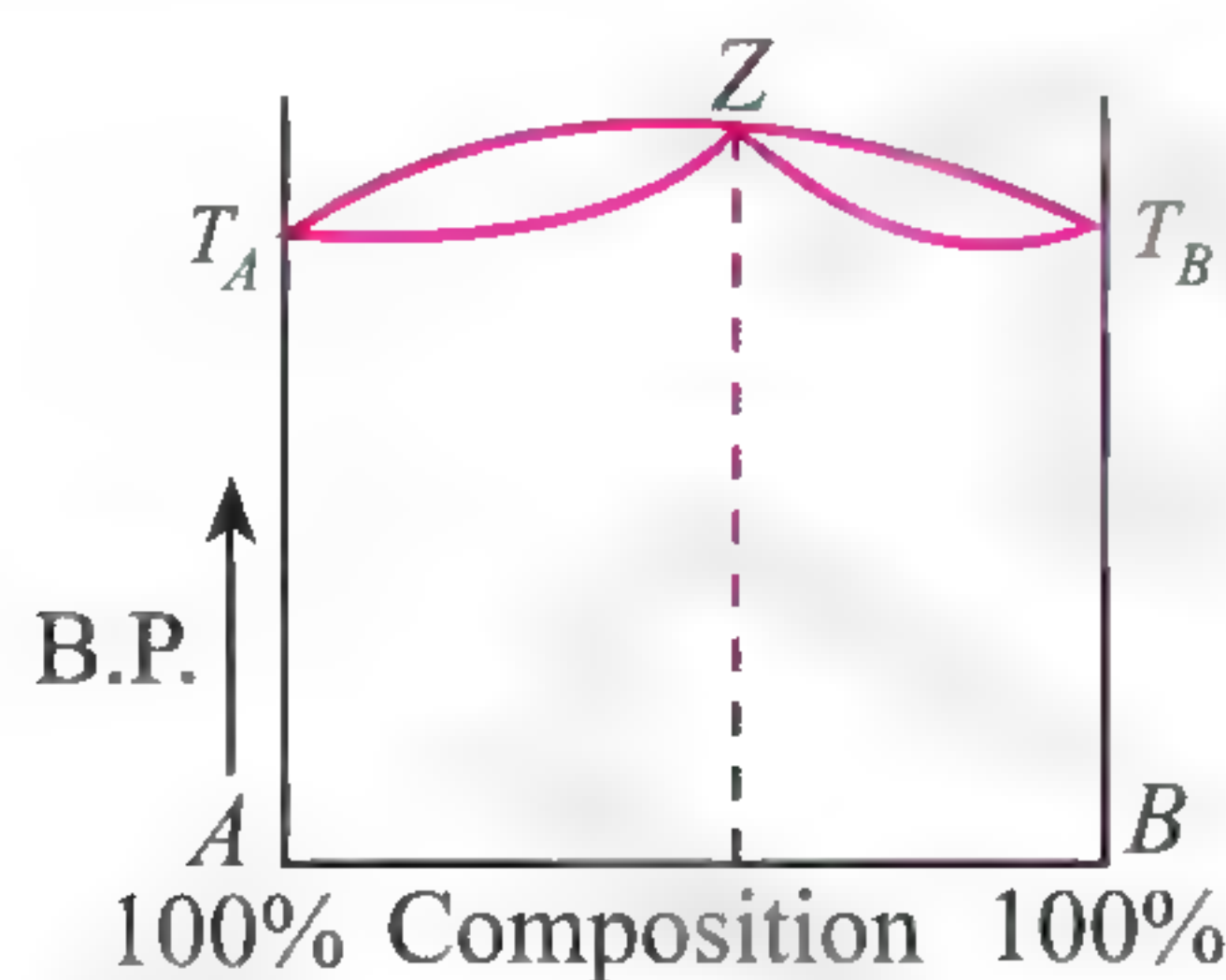
- (1) Heat of vaporisation for a pure solvent and for a solution are similar because similar intermolecular forces between solvent molecules must be overcome in both cases
- (2) Entropy change between solution and vapour is smaller than the entropy change between pure solvent and vapour
- (3) Boiling point of the solution is larger than that of the pure solvent
- (4) All are correct statements

55. Boiling point composition diagram of the liquid-vapour equilibrium for A and B is shown in the figure. If a binary liquid mixture of A and B is distilled fractionally, which of the following would be correct observation?



- (1) Composition of the still (residue) will approach pure liquid B only
- (2) Composition of the distillate will approach pure A only
- (3) Composition of distillate and residue will approach pure A and B respectively
- (4) Neither of the component can be obtained in pure state

56. A liquid mixture having composition corresponding to point Z in the figure shown is subjected to distillation at constant pressure. Which of the following statement is correct about the process?



- (1) The composition of distillate differs from the mixture
- (2) The boiling point goes on changing
- (3) The mixture has highest vapour pressure than for any other composition
- (4) Composition of an azeotrope alters on changing the external pressure

57. Which will form maximum boiling azeotrope?

- (1) $C_6H_6 + C_6H_5CH_3$ solution
- (2) $HNO_3 + H_2O$ solution

(3) $C_2H_5OH + H_2O$ solution

(4) n -hexane and n -heptane

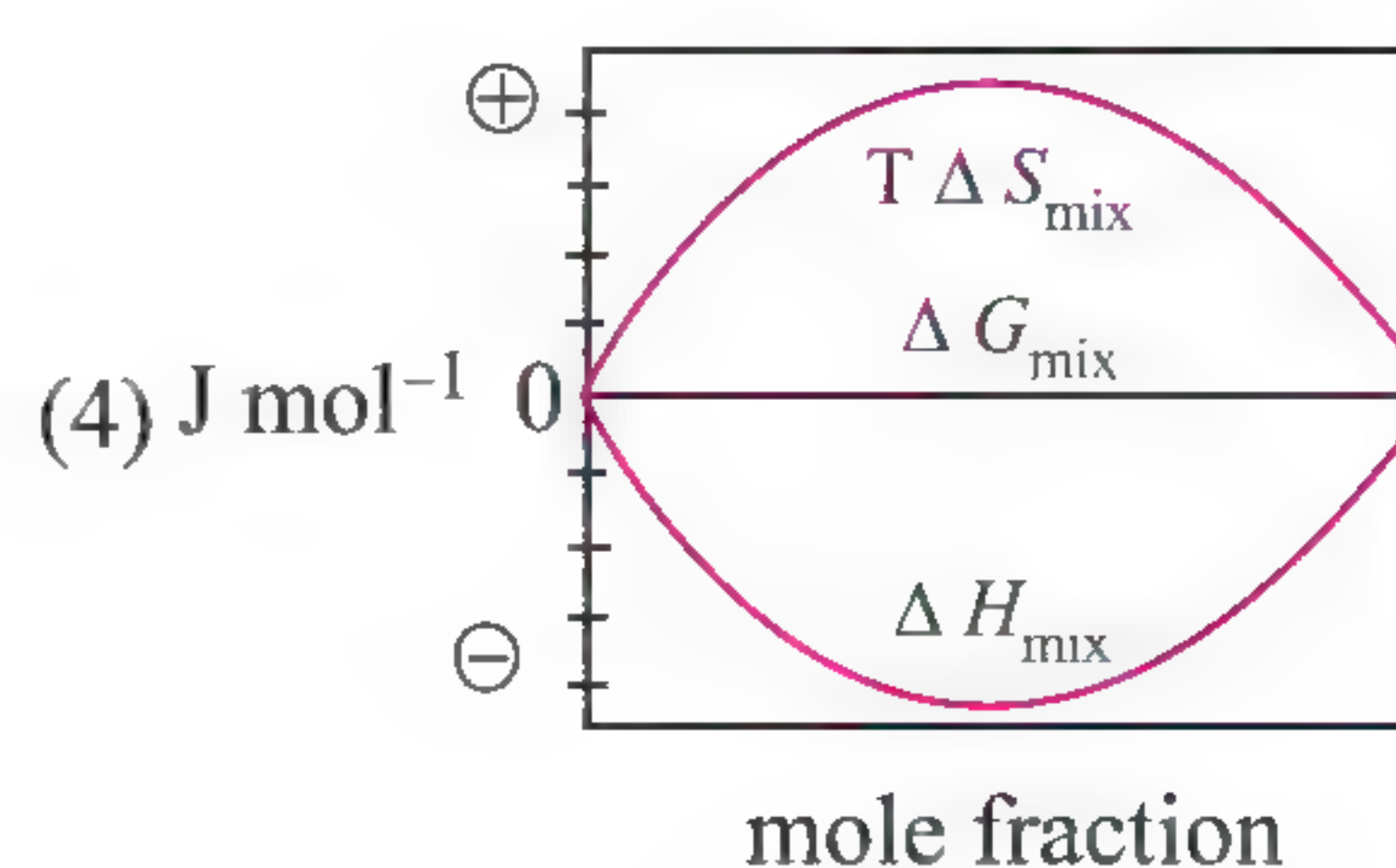
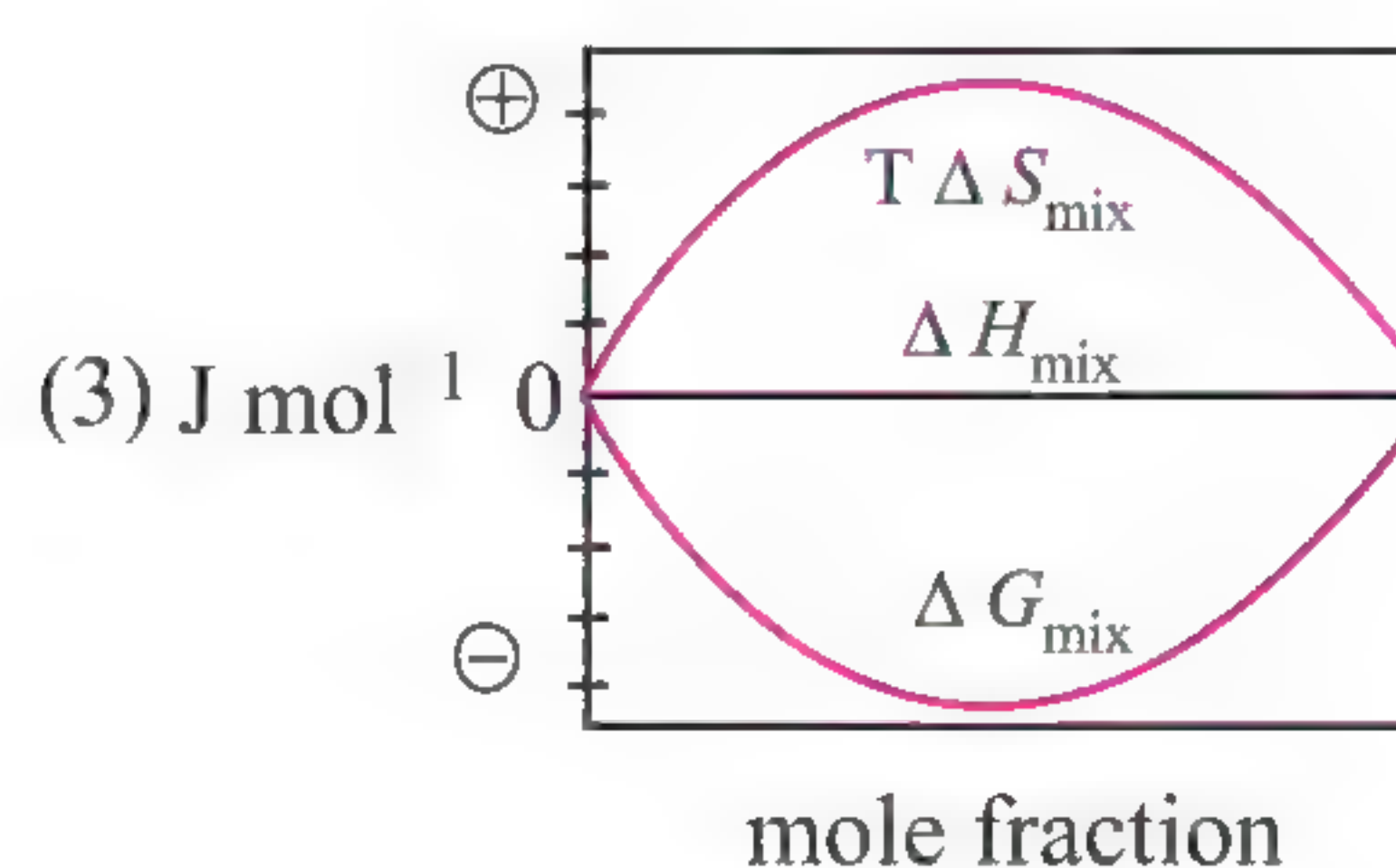
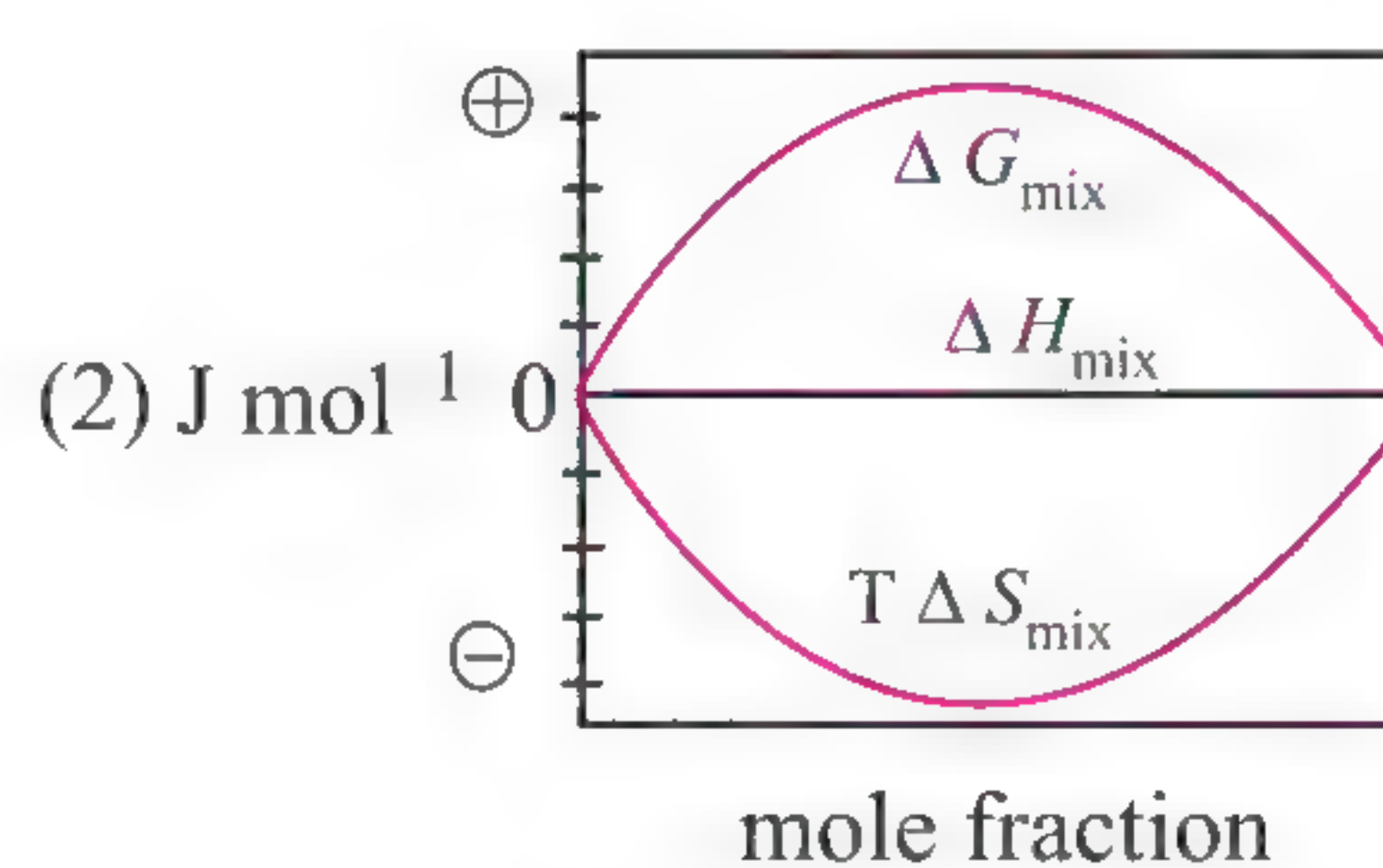
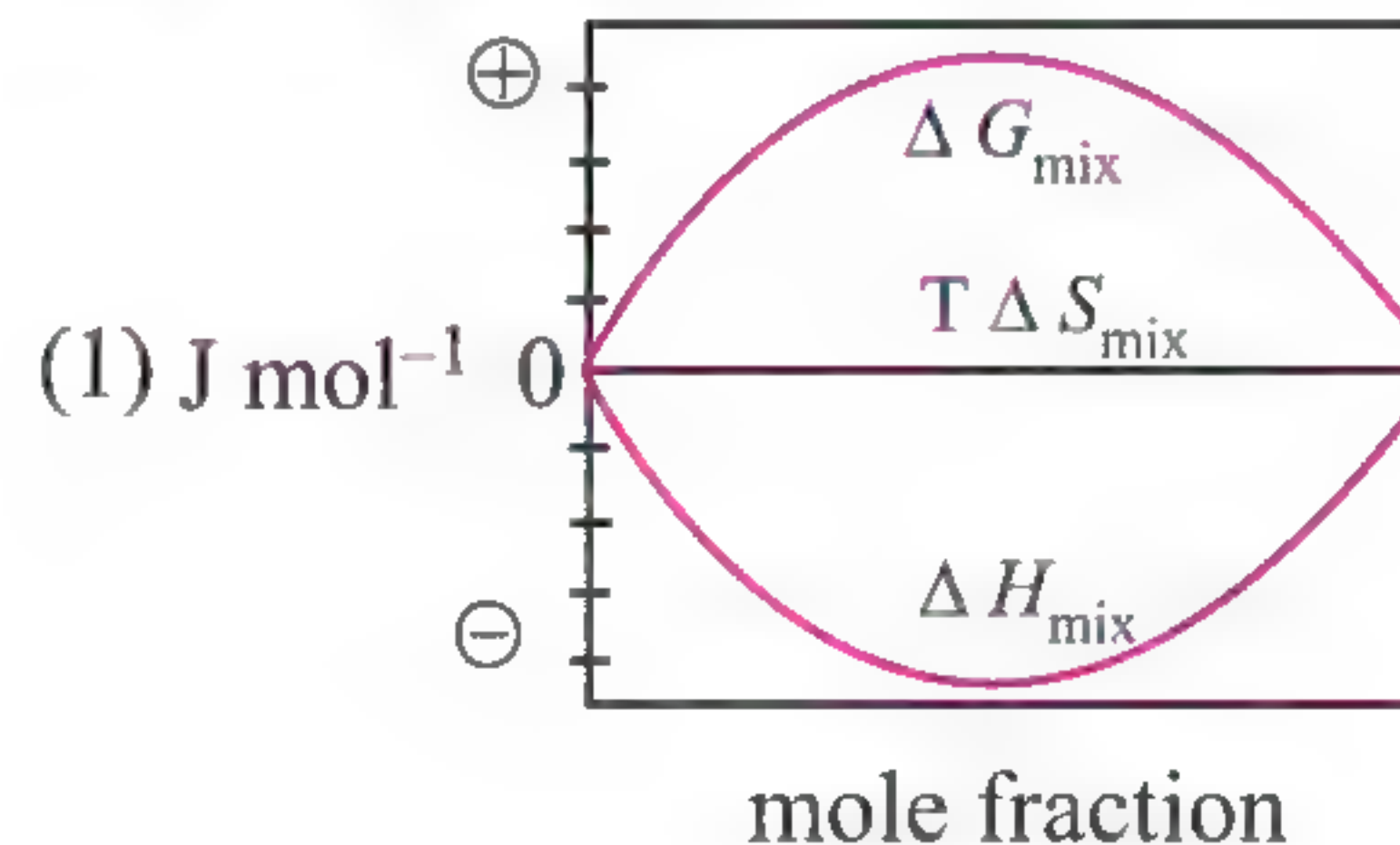
58. Total vapour pressure of mixture 1 mole of volatile component A ($P_A^\circ = 100$ mm Hg) and 3 mole of volatile component B ($P_B^\circ = 80$ mmHg) is 90 mm Hg. For such case:

- (1) There is positive deviation from Raoult's law
- (2) Boiling point has been lowered
- (3) Force of attraction between A and B is weaker than that between A and A or between B and B
- (4) All the above statements are correct

59. Two components A and B form an ideal solution. The mole fraction of A and B in ideal solution are X_A and X_B , while that of in vapour phase, these components have their mole fractions as Y_A and Y_B . Then, the slope and intercept of plot of $\frac{1}{Y_A}$ vs. $\frac{1}{X_A}$ will be:

- (1) $\frac{P_A^\circ}{P_B^\circ}, \frac{P_B^\circ - P_A^\circ}{P_B^\circ}$
- (2) $\frac{P_B^\circ}{P_A^\circ}, \frac{P_A^\circ - P_B^\circ}{P_A^\circ}$
- (3) $\frac{P_B^\circ}{P_A^\circ}, \frac{P_B^\circ}{P_B^\circ - P_A^\circ}$
- (4) $P_A^\circ - P_B^\circ, \frac{P_A^\circ}{P_B^\circ}$

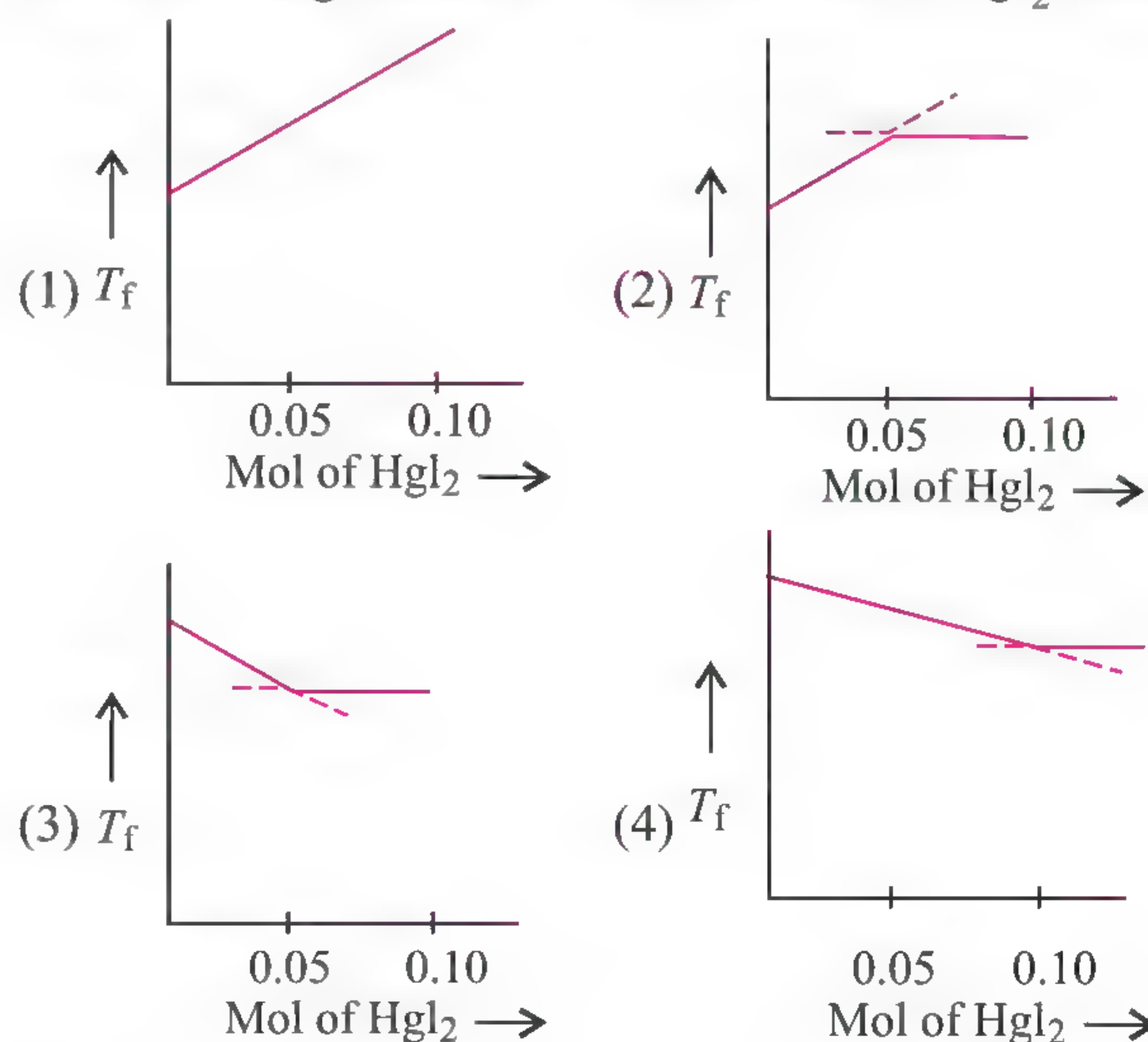
60. Which of the following represents correctly the changes in thermodynamic properties during the formation of 1 mole of an ideal binary solution?



61. 100 g of $\text{C}_6\text{H}_{12}\text{O}_6(\text{aq})$ solution has vapour pressure is equal to 40 torr at certain temperature. Vapour pressure of $\text{H}_2\text{O}(\text{l})$ is 40.18 torr at same temperature. If this solution is cooled to -0.93°C , what mass of ice will be separated out? ($K_f = 1.86 \text{ kg mol}^{-1}$)
- (1) 95.5 g (2) 4.5 g
(3) 45.5 g (4) 47.8 g

Colligative Properties and Vant Hoff Factor

62. An aqueous solution freezes at -2.55°C . What is its boiling point $K_{\text{b}}(\text{H}_2\text{O}) = 0.52 \text{ K m}^{-1}$; $K_{\text{f}}(\text{H}_2\text{O}) = 1.86 \text{ K m}^{-1}$?
- (1) 107.0°C (2) 100.6°C (3) 100.1°C (4) 100.7°C
63. The relative decrease in VP of an aqueous glucose dilute solution is found to be 0.018. Hence, the elevation in boiling point is (it is given 1 molal aqueous urea solution boils at 100.54°C at 1 atm pressure)
- (1) 0.018° (2) 0.18° (3) 0.54° (4) 0.03°
64. 10.0 g of glucose (π_1), 10.0 g of urea (π_2), and 10.0 g of sucrose (π_3) are dissolved in 250.0 mL of water at 273 K (π = osmotic pressure of a solution). The relationship between the osmotic pressure of the solutions is
- (1) $\pi_1 > \pi_2 > \pi_3$ (2) $\pi_3 > \pi_1 > \pi_2$
(3) $\pi_2 > \pi_1 > \pi_3$ (4) $\pi_2 > \pi_3 > \pi_1$
65. 0.6 g of a solute is dissolved in 0.1 L of a solvent which develops an osmotic pressure of 1.23 atm at 27°C . The molecular weight of the solute is
- (1) 149.5 g mol^{-1} (2) 120.0 g mol^{-1}
(3) 430.0 g mol^{-1} (4) None of these
66. A 5% solution of cane sugar (molecular weight = 342) is isotonic with a 1% solution of substance X. The molecular weight of X is
- (1) 342 (2) 171.12 (3) 65.6 (4) 136.8
67. What mass of urea be dissolved in 171 g of water so as to decrease the vapour pressure of water by 5%?
- (1) 15 g (2) 20 g (3) 25 g (4) 30 g
68. The vapour pressure at a given temperature of an ideal solution containing 0.2 mol of non-volatile solute and 0.8 mol of a solvent is 60 mm of Hg. The vapour pressure of the pure solvent at the same temperature will be
- (1) 120 mm Hg (2) 150 mm Hg
(3) 60 mm Hg (4) 75 mm Hg
69. The vapour pressure of a solution containing 5.0 g of a non-electrolyte in 100.0 g of water at a particular temperature is 2985 N m^{-2} . If the vapour pressure of pure water is 3000 N m^{-2} , the molecular weight of the solute is
- (1) 60.0 (2) 120.0
(3) 180.0 (4) 380.0
70. The molal boiling point constant for water is 0.513 K m^{-1} . When 0.1 mole of sugar is dissolved in 200.0 g of water, the solution boils under a pressure 1.0 atm at
- (1) 100.513°C (2) 100.0513°C
(3) 100.256°C (4) 101.025°C
71. What should be the boiling point of 1.0 molal aqueous KCl solution (assuming complete dissociation of KCl) if $K_{\text{b}}(\text{H}_2\text{O})$ is 0.52 K m^{-1} ?
- (1) 100.52°C (2) 101.04°C
(3) 99.48°C (4) 98.96°C
72. The ratio of freezing point depression values of 0.01 M solutions of urea, common salt, and Na_2SO_4 are
- (1) 1:1:1 (2) 1:2:1 (3) 1:2:3 (4) 2:2:3
73. From a measurement of the freezing point depression of benzene, the molecular weight of acetic acid in a benzene solution was determined to be 100. The percentage association of acetic acid is
- (1) 79% (2) 93% (3) 80% (4) 100%
74. An aqueous solution containing an ionic salt having molality equal to 0.19 freezes at -0.704°C . The Van't Hoff factor of the ionic salt is (K_{f} for water = 1.86 K m^{-1})
- (1) 3 (2) 2 (3) 4 (4) 5
75. The Van't Hoff factor for a 0.1 M $\text{Al}_2(\text{SO}_4)_3$ solution is 4.20. The degree of dissociation is
- (1) 80% (2) 90% (3) 78% (4) 83%
76. The degree of dissociation α of a weak electrolyte is
- (1) $\frac{i-1}{n+1}$ (2) $\frac{i-1}{n-1}$
(3) $\frac{n-1}{i-1}$ (4) $\frac{n+1}{i-1}$
- where n is the number of ions given by 1 mol of electrolyte.
77. Increasing amount of solid HgI_2 is added to 1 L of an aqueous solution containing 0.1 mol KI. Which of the following graphs do represent the variation of freezing point of the resulting solution with the amount of HgI_2 added?



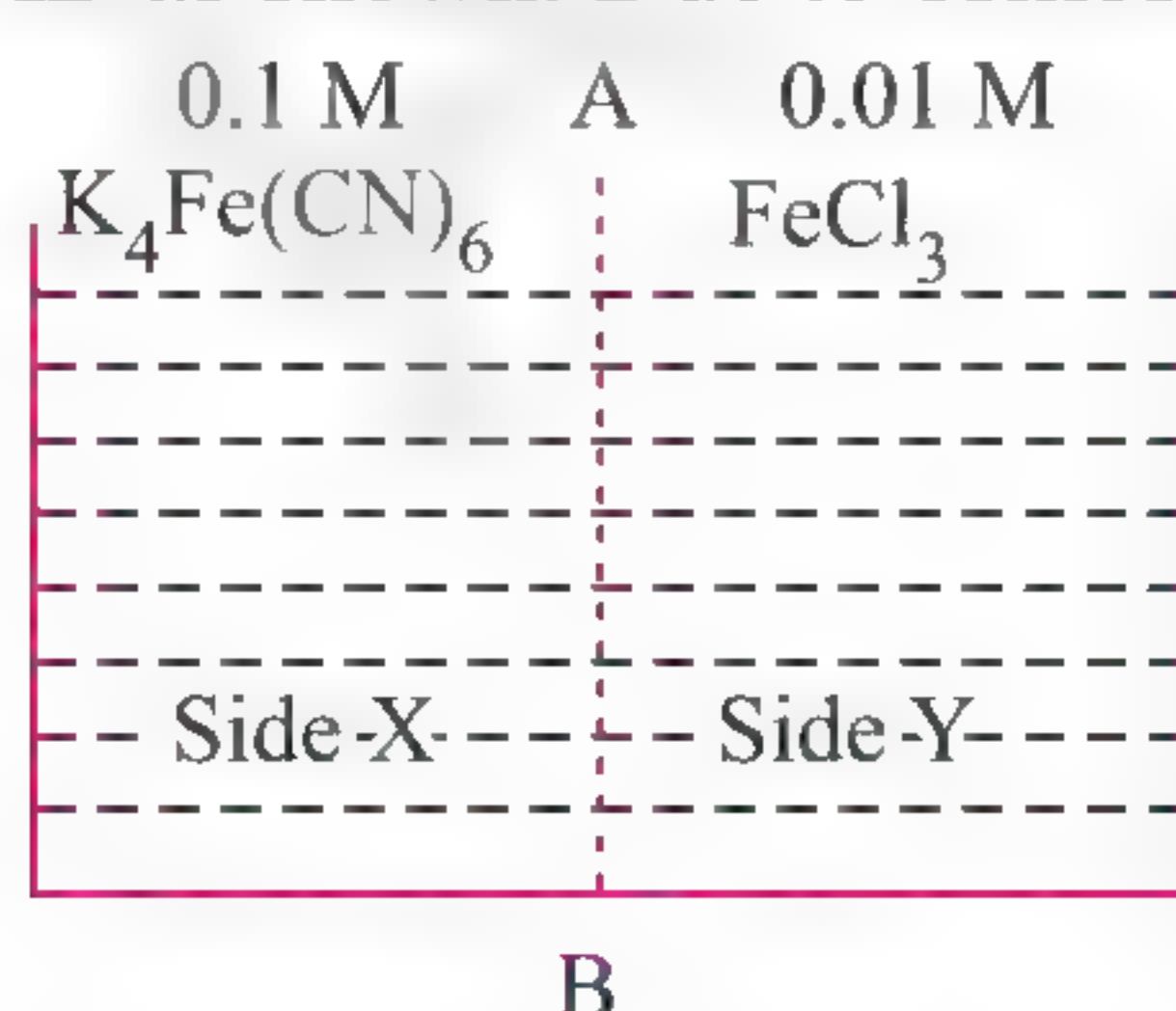
78. Equimolal solutions of KCl and compound X in water show depression in freezing point in the ratio of 4:1. Assuming KCl to be completely ionized, the compound X in solution must
- (1) Dissociate to the extent of 50%
(2) Hydrolyze to the extent of 80%
(3) Dimerize to the extent of 50%
(4) Trimerize to the extent of 75%

79. Arrange the following as directed: (Q.79–82)
Increasing order of boiling points.
I. 0.001 m NaCl II. 0.001 m urea
III. 0.001 m MgCl_2 IV. 0.001 m CH_3COOH
(1) $\text{II} < \text{IV} < \text{I} < \text{III}$ (2) $\text{II} < \text{I} < \text{IV} < \text{III}$
(3) $\text{III} < \text{I} < \text{IV} < \text{II}$ (4) $\text{III} < \text{IV} < \text{I} < \text{II}$
80. Increasing order freezing points.
I. 0.1 M ethanol II. 0.1 M $\text{Ba}_3(\text{PO}_4)_2$
III. 0.1 M Na_2SO_4
(1) $\text{II} < \text{III} < \text{I}$ (2) $\text{II} < \text{I} < \text{III}$
(3) $\text{I} < \text{III} < \text{II}$ (4) $\text{III} < \text{I} < \text{II}$
81. Increasing order of osmotic pressure.
I. 0.1 M glucose II. 1% urea solution
III. 0.1 M common salt
(1) $\text{III} < \text{II} < \text{I}$ (2) $\text{III} < \text{I} < \text{II}$
(3) $\text{I} < \text{II} < \text{III}$ (4) $\text{II} < \text{I} < \text{III}$
82. Increasing order of Van't Hoff factor.
I. NaNO_3 II. BaCl_2
III. $\text{K}_3[\text{Fe}(\text{CN})_6]$ IV. $\text{C}_6\text{H}_{12}\text{O}_6$
V. CH_3COOH
(1) $\text{III} < \text{I} < \text{V} < \text{IV} < \text{II}$ (2) $\text{IV} < \text{II} < \text{I} < \text{III} < \text{V}$
(3) $\text{III} < \text{II} < \text{I} < \text{V} < \text{IV}$ (4) $\text{IV} < \text{V} = \text{I} < \text{II} < \text{III}$
83. The use of common salts, e.g., NaCl or CaCl_2 anhydrous, is made to clear snow on the roads. This causes:
(1) A lowering in the freezing point of water.
(2) A lowering in the melting point of ice.
(3) Ice melts at the temperature of atmosphere present at that time.
(4) All of these.
84. The relative lowering of vapour pressure is equal to the mole fraction of the non-volatile solute. This statement was given by
(1) Raoult (2) Henry (3) Joule (4) Dalton
85. Assuming each salt to be 90% dissociated which of the following will have the highest osmotic pressure?
(1) Decinormal $\text{Al}_2(\text{SO}_4)_3$
(2) Decinormal BaCl_2
(3) Decinormal Na_2SO_4
(4) A solution obtained by mixing equal volumes of (2) and (3) and filtering
86. When a solution is separated from a solvent by a semi-permeable membrane, then the phenomenon taking place is called as
(1) Osmosis (2) Diffusion (3) Solubility (4) None
87. If a thin slice of sugar beet is placed in concentrated solution of NaCl , then
(1) Sugar beet will lose water from its cells.
(2) Sugar beet will absorb water from solution.
(3) Sugar beet will neither absorb nor lose water.
(4) Sugar beet will dissolve in solution.
88. Which salt shows maximum osmotic pressure in its 1 m solution?
(1) AgNO_3 (2) Na_2SO_4 (3) $(\text{NH}_4)_3\text{PO}_4$ (4) MgCl_2
89. Which solution will show maximum elevation in boiling point?
(1) 0.1 M KCl (2) 0.1 M BaCl_2
(3) 0.1 M FeCl_3 (4) 0.1 M $\text{Fe}_2(\text{SO}_4)_3$
90. When common salt is dissolved in water
(1) The melting point of the solution increases.
(2) The boiling point of solution decreases.
(3) Both melting point and boiling point decrease.
(4) The boiling point of the solution increases.
91. A teacher one day pointed out to his students the peculiar fact that water is a unique liquid which freezes exactly at 0°C and boils exactly at 100°C . He asked the students to find the correct statement based on this fact.
(1) Water dissolves anything, however sparingly the dissolution may be.
(2) Water is a polar molecule.
(3) Boiling and freezing temperatures of water were used to define a temperature scale.
(4) Liquid water is denser than ice.
92. The osmotic pressure of a dilute solution is directly proportional to the
(1) Diffusion rate of the solute
(2) Ionic concentration
(3) Boiling point
(4) Flow of solvent from a concentrated solution
93. The freezing point of 1% aqueous solution of calcium nitrate will be
(1) 0°C (2) Above 0°C
(3) 1°C (4) Below 0°C
94. A perfectly semi-permeable membrane when used to separate a solution from its solvent permits through it the passage of
(1) Solute only (2) Solvent only
(3) Both (1) and (2) (4) None
95. Which statement is incorrect about osmotic pressure (π), volume (V), and temperature (T)?
(1) $\pi \propto \frac{1}{V}$, if T is constant.
(2) $\pi \propto T$, if V is constant.
(3) $\pi \propto V$, if T is constant.
(4) πV is constant, if T is constant.
96. Semi-permeable membrane is chemically
(1) Copper ferrocyanide
(2) Copper ferricyanide
(3) Copper sulphate
(4) Potassium ferrocyanide
97. The depression in freezing point is maximum if the solvent used is
(1) Camphor (2) Naphthalene
(3) Benzene (4) Water

98. The osmotic pressure of a dilute solution is given by
 (1) $P = P_0 \times N_1$ (2) $\pi V = nRT$
 (3) $\Delta P = P_0 N_2$ (4) $\frac{\Delta P}{P^\circ} = \frac{P^\circ - P_s}{P^\circ}$
99. Which is not a colligative property?
 (1) Lowering of vapour pressure
 (2) Freezing point
 (3) Osmotic pressure
 (4) Elevation in boiling point
100. Blood has been found to be isotonic with
 (1) Normal saline solution
 (2) Saturated NaCl solution
 (3) Saturated KCl solution
 (4) Saturated solution of a 1 : 1 mixture of NaCl and KCl
101. Isotonic solutions are those which have
 (1) Same osmotic pressure
 (2) Same molarity
 (3) Same density
 (4) Same normality
102. The correct relationship between the boiling points of very dilute solutions of AlCl_3 (t_1) and CaCl_2 (t_2), having the same molar concentration, is
 (1) $t_1 = t_2$ (2) $t_1 > t_2$ (3) $t_2 > t_1$ (4) $t_2 \geq t_1$
103. Two solutions of KNO_3 and CH_3COOH are prepared separately. The molarity of both is 0.1 M and osmotic pressure is P_1 and P_2 , respectively.
 The correct relationship between the osmotic pressures is
 (1) $P_2 > P_1$ (2) $P_1 = P_2$
 (3) $P_1 > P_2$ (4) $\frac{P_1}{P_1 + P_2} = \frac{P_2}{P_1 + P_2}$
104. Boiling point elevation is
 (1) Additive property
 (2) Constitutive property
 (3) Colligative property
 (4) Partly additive and partly constitutive
105. An example of colligative property is
 (1) Freezing point (2) Boiling point
 (3) Vapour pressure (4) Osmotic pressure
106. The colligative properties of a solution depend on
 (1) The number of solute particles present in it
 (2) The chemical nature of the solute particles present in it
 (3) The nature of the solvent used
 (4) None of these
107. Osmosis is the spontaneous flow through a semi-permeable membrane of
 (1) A less concentrated solution into more concentrated solution
 (2) The solvent from a solution of lower concentration to one of higher concentration
 (3) Solute particles from a solution of higher concentration to one of lower concentration
 (4) None of these
108. The osmotic pressure of a non-aqueous solution is measured by
 (1) Berkeley and Hartley method
 (2) Pfeffer's method
 (3) Morse and Frazer method
 (4) Townend's method
109. The osmotic pressure of a solution increases if
 (1) Temperature is lowered
 (2) Volume is increased
 (3) Number of solute molecules is increased
 (4) None of these
110. The ratio of the value of any colligative property for KCl solution to that of sugar solution is
 (1) 1 (2) 0.5 (3) 2 (4) 4
111. Equimolal solutions A and B show depression in freezing point in the ratio 2 : 1. A remains in the normal state in solution. B will be
 (1) Normal in solution (2) Dissociated in solution
 (3) Associated in solution (4) Hydrolysed in solution
112. The vapour pressure (VP) of a dilute solution of non-volatile solute is P and the VP of a pure solvent is P° . The lowering of the VP is
 (1) +ve (2) -ve (3) P/P° (4) P°/P
113. The value of K_f for water is 1.86° , calculated from glucose solution. The value of K_f for water calculated for NaCl solution will be
 (1) $=1.86$ (2) <1.86 (3) >1.86 (4) Zero
114. What will be the molecular weight of NaCl determined experimentally following elevation in the boiling point or depression in freezing point method?
 (1) <58.5 (2) >58.5 (3) $=58.5$ (4) None
115. The Van't Hoff factor of NaCl assuming 100% dissociation is
 (1) $1/2$ (2) 2 (3) 1 (4) 3
116. The solutions in which the blood cells retain their normal shape, with regard to the blood, are
 (1) Isotonic (2) Hypertonic
 (3) Hypotonic (4) None of these
117. The factor $\Delta T_f/K_f$ represents
 (1) Molarity (2) Formality (3) Normality (4) Molality
118. Which of the following solutions has minimum freezing point?
 (1) 0.01M NaCl (2) 0.005 M $\text{C}_2\text{H}_5\text{OH}$
 (3) 0.005 M MgI_2 (4) 0.005 M MgSO_4
119. Which of the following solutions will have the highest boiling point?
 (1) 1% glucose in water (2) 1% sucrose in water
 (3) 1% NaCl in water (4) 1% CaCl_2 in water

120. Which of the following solutions has the minimum freezing point?
 (1) 1 molal NaCl solution (2) 1 molal KCl solution
 (3) 1 molal CaCl_2 solution (4) 1 molal urea solution
121. The osmotic pressure of equimolar solutions of BaCl_2 , NaCl, and glucose follow the order
 (1) $\text{BaCl}_2 > \text{NaCl} > \text{Glucose}$
 (2) $\text{Glucose} > \text{NaCl} > \text{BaCl}_2$
 (3) $\text{NaCl} > \text{BaCl}_2 > \text{Glucose}$
 (4) $\text{NaCl} > \text{Glucose} > \text{BaCl}_2$
122. Which of the following solutions has the maximum freezing point?
 (1) 1 molar of NaCl solution
 (2) 1 molar of KCl solution
 (3) 1 molar of CaCl_2 solution
 (4) 1 molar of urea solution
123. The osmotic pressure of a 5% (weight/volume) solution of cane sugar at 150°C is
 (1) 4 atm (2) 3.4 atm (3) 5.078 atm (4) 2.45 atm
124. The freezing point of a 0.05 molal solution of non-electrolyte in water is
 ($K_f = 1.86 \text{ K m}^{-1}$)
 (1) -1.86°C (2) -0.93°C (3) -0.093°C (4) 0.093°C
125. The freezing point of 1 m NaCl solution assuming NaCl to be 100% dissociated in water is ($K_f = 1.86 \text{ K m}^{-1}$)
 (1) -1.86°C (2) -3.72°C (3) $+1.86^\circ\text{C}$ (4) $+3.72^\circ\text{C}$
126. The molal freezing point constant of water is 1.86 K m^{-1} . If 342 g of cane sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) is dissolved in 1000 g of water, the solution will freeze at
 (1) -1.86°C (2) 1.86° (3) -3.92°C (4) 2.42°C
127. The osmotic pressure of a solution containing 0.1 mol of solute per litre at 273 K is
 (1) $\frac{0.1}{1} \times 0.08205 \times 273 \text{ atm}$
 (2) $0.1 \times 2 \times 0.08205 \times 273 \text{ atm}$
 (3) $\frac{1}{0.1} \times 0.08205 \times 273 \text{ atm}$
 (4) $\frac{0.1}{1} \times \frac{273}{0.08205} \text{ atm}$
128. The osmotic pressure of 40% (weight/volume) urea solution is 1.64 atm and that of 3.42% (weight/volume) cane sugar is 2.46 atm. When equal volumes of the above two solutions are mixed, the osmotic pressure of the resulting solution is
 (1) 1.64 atm (2) 2.46 atm (3) 4.10 atm (4) 2.05 atm
129. The osmotic pressure of a solution (density is 1 g mL^{-1}) containing 3 g of glucose (molecular weight = 180) in 60 g of water at 15°C is
 (1) 0.34 atm (2) 0.65 atm (3) 6.25 atm (4) 5.57 atm
130. What would be the freezing point of aqueous solution containing 17 g of $\text{C}_2\text{H}_5\text{OH}$ in 1000 g of water. $K_{f\text{H}_2\text{O}} = 1.86 \text{ K m}^{-1}$.
 (1) -0.69°C (2) -0.34°C
 (3) 0.0°C (4) 0.34°C
131. A solution containing 8.6 g urea in 1 L was found to be isotonic with a 5% (weight/volume) solution of an organic non-volatile solute. The molecular weight of latter is
 (1) 348.9 (2) 34.89 (3) 3489 (4) 861.2
132. A solution containing 4 g of a non-volatile organic solute per 100 mL was found to have an osmotic pressure equal to 500 cm of mercury at 27°C . The molecular weight of solute is
 (1) 14.97 (2) 149.7 (3) 1697 (4) 1.497
133. The molal elevation constant of water = 0.52 K m^{-1} . The boiling point of 1.0 molal aqueous KCl solution (assuming complete dissociation of KCl) should be
 (1) 100.52°C (2) 101.04°C
 (3) 99.48°C (4) 98.96°C
134. If a 6.84% (weight/volume) solution of cane sugar (molecular weight = 342) is isotonic with 1.52% (weight/volume) solution of thiocarbamide, then the molecular weight of thiocarbamide is
 (1) 152 (2) 760 (3) 60 (4) 180
135. The osmotic pressure of a sugar solution at 24°C is 2.5 atm. The concentration of the solution in mole per litre is
 (1) 10.25 (2) 1.025 (3) 1025 (4) 0.1025
136. The Van't Hoff factor of very dilute solution of $\text{Ca}(\text{NO}_3)_2$ is
 (1) 1 (2) 2 (3) 3 (4) 4
137. Lowering in vapour pressure is highest for
 (1) 0.2 m urea (2) 0.1 m glucose
 (3) 0.1 m MgSO_4 (4) 0.1 m BaCl_2
138. Which of the following will have the highest boiling point at 1 atm pressure?
 (1) 0.1 M NaCl (2) 0.1 M sucrose
 (3) 0.1 M BaCl_2 (4) 0.1 M glucose
139. An aqueous solution freezes at -0.186°C ($K_f = 1.86^\circ$; $K_b = 0.512^\circ$). What is the elevation in boiling point?
 (1) 0.186 (2) 0.512 (3) $\frac{0.512}{1.86}$ (4) 0.0512
140. The molal depression constant for water is 1.86°C . The freezing point of a 0.05-molal solution of a non-electrolyte in water is
 (1) -1.86°C (2) -0.93°C (3) -0.093°C (4) 0.93°C
141. The freezing point of a solution prepared from 1.25 g of non-electrolyte and 20 g of water is 271.9 K. If the molar depression constant is 1.86 K mol^{-1} , then molar mass of the solute will be
 (1) 105.7 (2) 106.7
 (3) 115.3 (4) 93.9

142. A 5% solution of cane sugar (molecular weight = 342) is isotonic with 1% solution of substance X. The molecular weight of X is
 (1) 171.2 (2) 68.4 (3) 34.2 (4) 136.2
143. The osmotic pressure of blood is 7.40 atm at 27°C. The number of mol of glucose to be used per litre for an intravenous injection that is to have the same osmotic pressure as blood is
 (1) 0.3 (2) 0.2 (3) 0.1 (4) 0.4
144. $\text{PtCl}_4 \cdot 6\text{H}_2\text{O}$ can exist as a hydrated complex; 1 m aqueous solution has the depression in freezing point of 3.72 K. Assume 100% ionization and $K_f(\text{H}_2\text{O}) = 1.86 \text{ K m}^{-1}$, then the complex is
 (1) $[\text{Pt}(\text{H}_2\text{O})_6]\text{Cl}_4$ (2) $[\text{Pt}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$
 (3) $[\text{Pt}(\text{H}_2\text{O})_3\text{Cl}_3]\text{Cl} \cdot 3\text{H}_2\text{O}$ (4) $[\text{Pt}(\text{H}_2\text{O})_2\text{Cl}_4] \cdot 4\text{H}_2\text{O}$
145. Which of the following solutions (1 molal) will have the maximum freezing point, assuming equal ionization in each case?
 (1) $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_3$ (2) $[\text{Fe}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$
 (3) $[\text{Fe}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ (4) $[\text{Fe}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$
146. The depression in freezing point of 0.01 m aqueous CH_3COOH solution is 0.02046° . 1 m urea solution freezes at -1.86°C . Assuming molality equal to molarity, pH of CH_3COOH solution is
 (1) 2 (2) 3 (3) 3.2 (4) 4.2
147. pH of a 0.1 M monobasic acid is found to be 2. Hence, its osmotic pressure at a given temperature T K is
 (1) $0.1RT$ (2) $0.11RT$ (3) $1.1RT$ (4) $0.01RT$
148. The lowering of vapour pressure due to a solute in a 1 m aqueous solution at 100°C is
 (1) 13.44 torr (2) 14.12 torr
 (3) 312 torr (4) 352 torr
149. Which has the maximum osmotic pressure at temperature T ?
 (1) 100 mL of 1 M urea solution.
 (2) 300 mL of 1 M glucose solution.
 (3) Mixture of 100 mL of 1 M urea solution and 300 mL of 1 M glucose solution.
 (4) All are isotonic.
150. FeCl_3 on reaction with $\text{K}_4[\text{Fe}(\text{CN})_6]$ in aqueous solution gives blue colour. These are separated by a semi-permeable membrane AB as shown. Due to osmosis, there is



- (1) Blue colour formation in side X.
 (2) Blue colour formation in side Y.
 (3) Blue colour formation in both of sides X and Y.
 (4) No blue colour formation.

151. 12.2 g of benzoic acid ($M_w = 122$) in 100 g benzene has depression in freezing point 2.6° ; $K_f = 5.2^\circ \text{ kg mol}^{-1}$. If there is 100% polymerization, the number of molecules of benzoic acid in associated state is
 (1) 1 (2) 2 (3) 3 (4) 4
152. 25 mL of an aqueous solution of KCl was found to require 20 mL of 1 M AgNO_3 solution when titrated using a K_2CrO_4 as indicator. The depression in freezing point of KCl solution with 100% ionization will be:
 $[K_f = 2.0^\circ \text{ mol}^{-1} \text{ kg and molarity = molality}]$
 (1) 5.0° (2) 3.2° (3) 1.6° (4) 0.8°

For Problems 153–155

Following questions are based on the following activities (A) with observations (O) and results or reason (R),

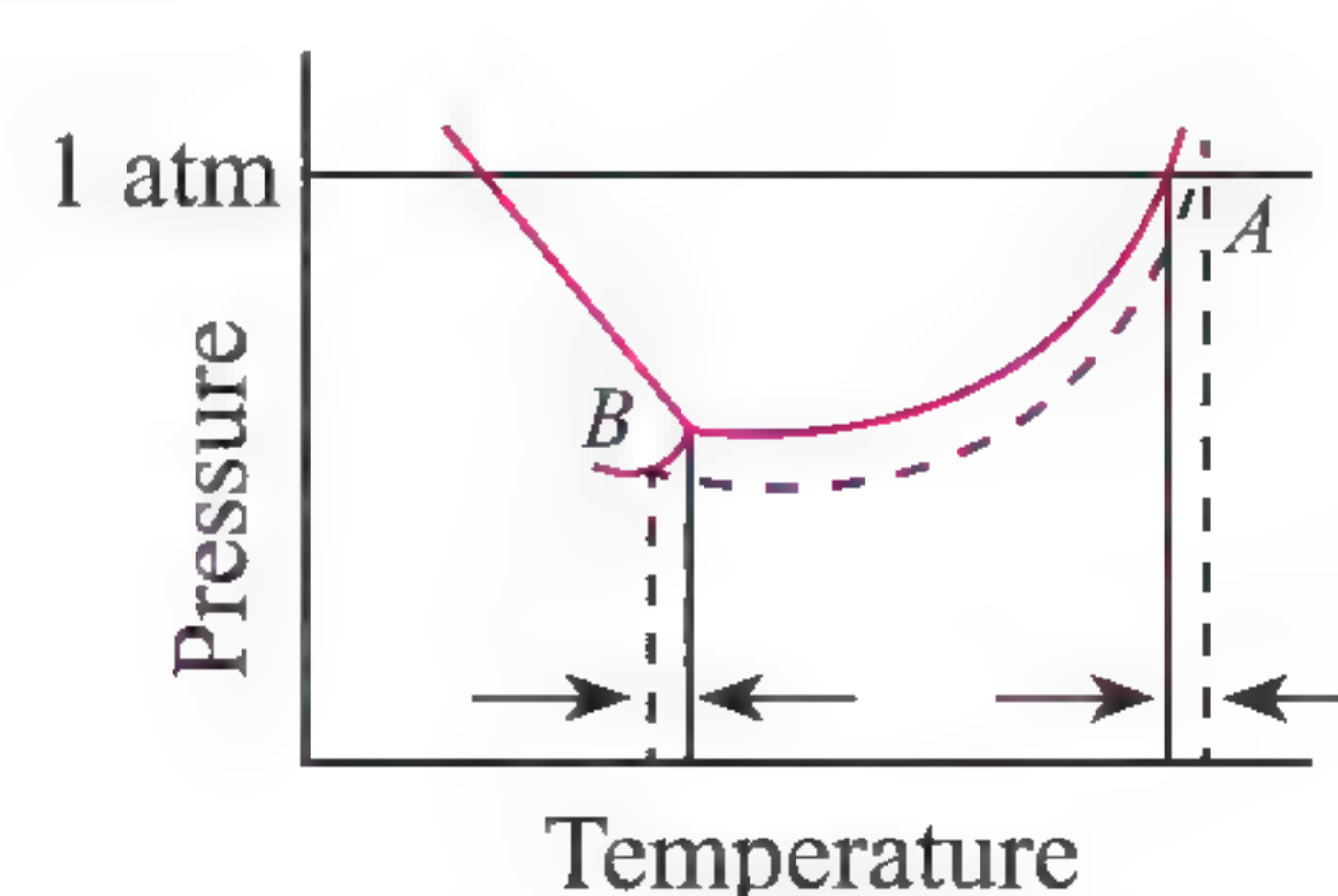
- (1) If A and O are correct and R is incorrect, mark (1).
 (2) If A and O are incorrect and R is correct, mark (2).
 (3) If A, O, and R are all correct, mark (3).
 (4) If A is correct, and O and R are incorrect, mark (4).

	Activity (A)	Observation (O)	Result/ reason (R)
153.	0.01 M $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 0.1 M FeCl_3 solutions are separated by a semi-permeable membrane.	Osmosis takes place from 0.01 M solution to 0.1 M solution but no blue colour formation either of side.	Osmosis takes place from dilute to concentrated solution and the solvent (H_2O) that flows.
154.	1 mol each of benzene and toluene are mixed.	$P_{\text{total}}^\circ = P_B^\circ \chi_B + P_T^\circ \chi_T$	This is positive deviation from Raoult's law.
155.	Ether is added to H_2O .	Boiling point is elevated	Boiling point is elevated when a volatile solute is added to a solvent.

156. The amount of ice that will separate out on cooling a solution containing 50 g of ethylene glycol in 200 g water to -9.3°C is: ($K'_f = 1.86 \text{ K molality}^{-1}$)

- (1) 38.71 g (2) 38.71 mg
 (3) 42 g (4) 42 mg

157. The phase diagrams for a pure solvent (represented by the solid line) and a corresponding solution (containing a nonvolatile solute and represented by the dashed lines) are shown below.



168. Select the INCORRECT statement about solubility of gases and Henry's constant:

- (1) Partial pressure of a gas is related to number of moles of the dissolved gas and K_H (Henry's constant)
- (2) $O_2(g)$ and $N_2(g)$ are less soluble in H_2O and solubility of these gases decrease with increase of temperature. These gases have higher K_H value at a given pressure and K_H value increase with temperature
- (3) $SO_2(g)$ and $NH_3(g)$ are more soluble in H_2O and solubility of these gases decrease with increase of temperature. These gases have lower K_H value at a given pressure.
- (4) Helium (g) and Argon (g) are sparingly soluble in acetone and solubility of these gases increases slightly with increase of temperature. These gases have higher K_H value at a given pressure.

169. The van't Hoff factor (i) for the following are respectively, if 60% ionisation or association takes place.

I. Hg_2Cl_2 in aqueous solution.

II. Boron in non-aqueous solution

- (1) 2.2, 0.45 (2) 0.54
- (3) 2.8, 0.55 (4) 3, 0.5

170. If the boiling point of an aqueous solution is $100.3^\circ C$. Given l_f and l_v are 100 and 500 cal g^{-1} respectively. (l_f and l_v are latent heat of fusion and vapourization respectively)

Select the CORRECT expression for ΔT_f

- (1) $\Delta T_f = \frac{(273)^2 \times 1.5}{(373)^2}$ (2) $\Delta T_f = \frac{(273)^2 \times 0.5}{(373)^2}$
- (3) $\Delta T_f = \frac{(373)^2 \times 1.5}{(273)^2}$ (4) $\Delta T_f = \frac{(373)^2 \times 0.5}{(273)^2}$

Multiple Correct Answers Type

Raoult's Law, Ideal and NonIdeal Solution, Azeotrope

1. Two miscible liquids A and B having vapour pressure in pure state P_A° and P_B° are mixed in mole fraction χ_A and χ_B to get a mixture having total vapour pressure of mixture P_M . Which of the following relations are correct?

- (1) $\chi_A = \frac{P_M - P_B^\circ}{P_A^\circ - P_B^\circ}$ (2) $\frac{\chi_{A(l)}}{\chi'_{A(v)}} = \frac{P_M}{P_A^\circ}$
- (3) $\frac{\chi_{A(l)}}{\chi'_{A(v)}} = \frac{P_M}{P_B^\circ}$ (4) All of these

2. A mixture of two immiscible liquids A and B, having vapour pressure in pure state obeys the following relationship if χ_A and χ_B are mole fractions of A and B in vapour phase over the solution

- (1) $P'_A = P_M \chi'_A$
- (2) $\frac{P'_A}{P'_B} = \frac{W_A \times M_{wB}}{M_{wA} \times W_B}$

(3) If $P'_A > P'_B$ then $\chi'_A < \chi'_B$

(4) If $P'_A > P'_B$, then $n_A > n_B$

3. Which relations are not correct for an aqueous dilute solution of K_3PO_4 if its degree of dissociation is α ?

$$(1) \frac{\Delta P}{P^\circ} = \frac{\text{Molality} \times 18 \times (1 + 3\alpha)}{1000}$$

$$(2) \frac{\Delta P}{P^\circ} = \frac{\pi_{\text{obs}} \times 18 \times (1 + 3\alpha)}{RT \times 1000}$$

$$(3) \frac{\Delta P}{P^\circ} = \frac{\Delta T_{f\text{obs}} \times 18}{K_f \times 1000}$$

$$(4) M_w \text{ of } K_3PO_4 = M_{w\text{obs}} \times (1 + 3\alpha)$$

4. Which of the following statements is/are correct?

- (1) Minimum boiling azeotropic mixture boils at temperature lower than either of the two pure components.
- (2) Maximum boiling azeotropic mixture boils at temperature higher than either of the two pure components.
- (3) Minimum boiling azeotropic mixture shows positive deviation.
- (4) Maximum boiling azeotropic mixture shows negative deviation.

5. For a non-volatile solute

- (1) The vapour pressure of a solute is zero.
- (2) Vapour pressure of solution = Vapour pressure of pure solvent.
- (3) Vapour pressure of solution = Vapour pressure of solvent in solution.
- (4) All of these.

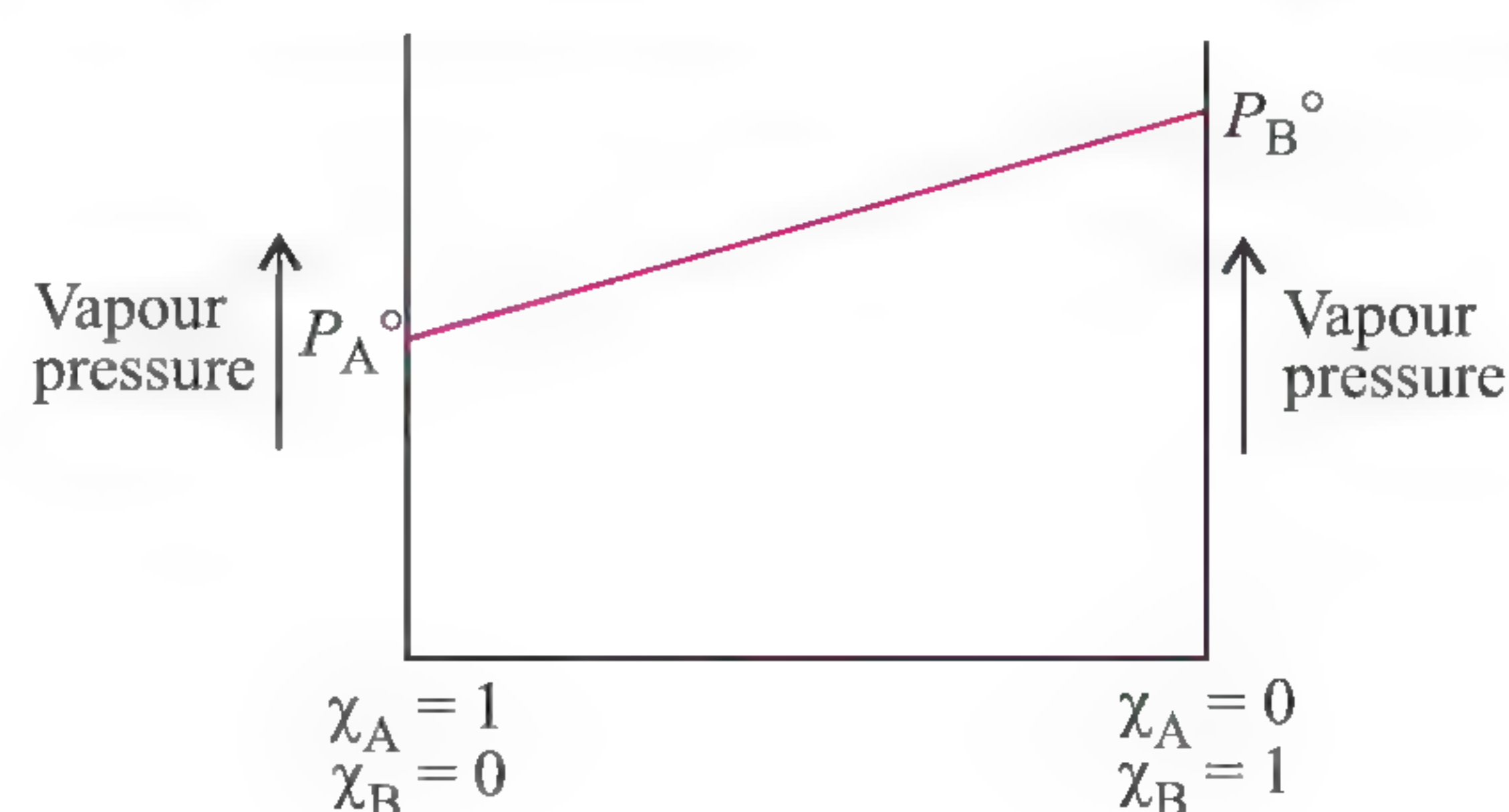
6. 1 mol benzene ($P^\circ_{\text{benzene}} = 42 \text{ mm}$) and 2 mol toluene ($P^\circ_{\text{toluene}} = 36 \text{ mm}$) will have

- (1) Total vapour pressure of 38 mm.
- (2) Mole fraction of vapour of benzene above liquid mixture is 7/19.
- (3) Positive deviation from Raoult's law.
- (4) Negative deviation from Raoult's law.

7. Which pair(s) of liquids on mixing is/are expected to show no net volume change and no heat effect?

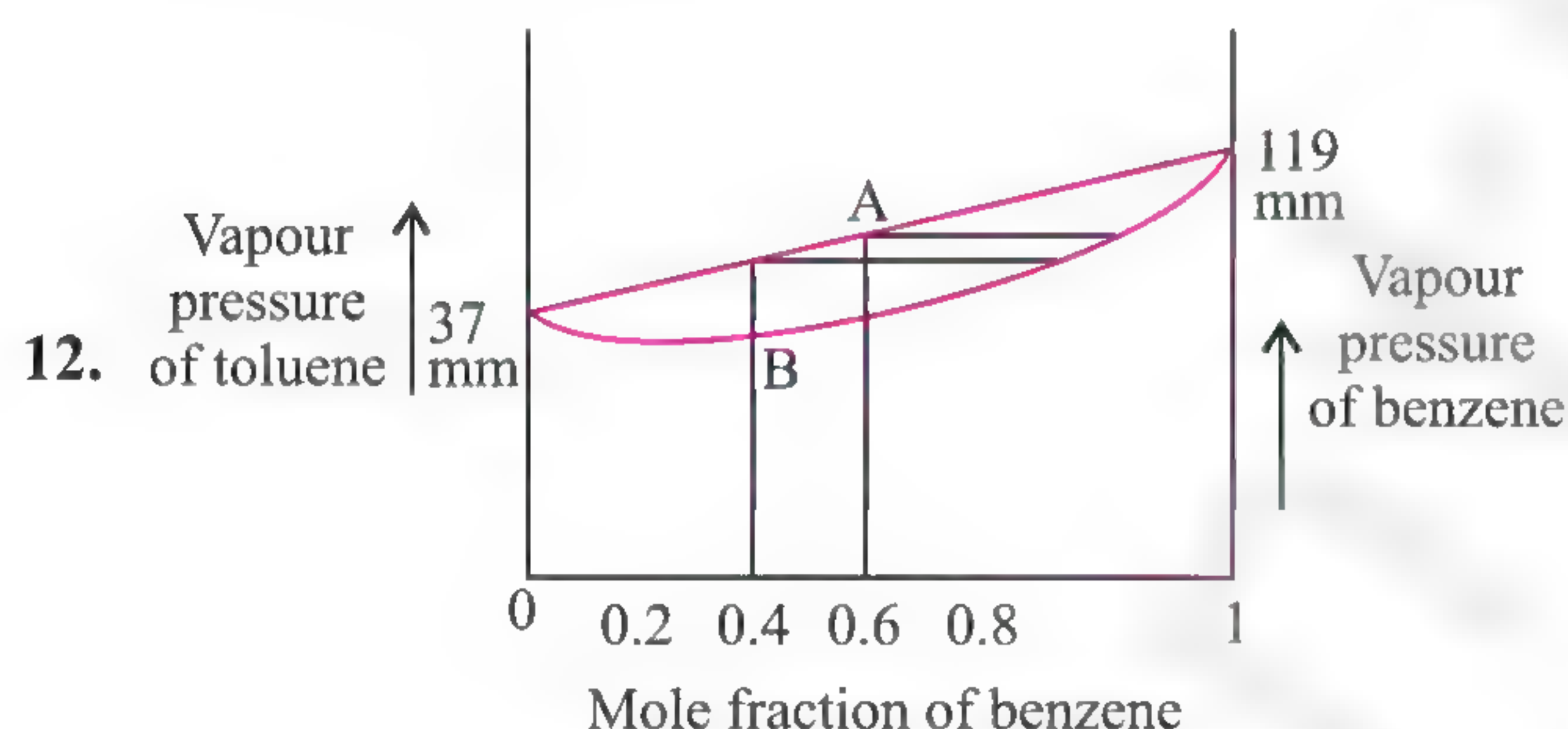
- (1) Acetone and ethanol
- (2) Chlorobenzene and bromobenzene
- (3) Chloroform and benzene
- (4) *n*-Butyl chloride and *n*-butyl bromide

8. The following is a graph plotted between the vapour pressure of two volatile liquids against their respective mole fractions.



Which of the following statements is/are correct?

- (1) When $\chi_A = 1$ and $\chi_B = 0$, then $P = P_A^\circ$.
 - (2) When $\chi_B = 1$ and $\chi_A = 0$, then $P = P_B^\circ$.
 - (3) When $\chi_A = 1$ and $\chi_B = 0$, then $P < P_B^\circ$.
 - (4) When $\chi_B = 1$ and $\chi_A = 0$, then $P > P_A^\circ$.
9. Which of the following combinations are correct for a binary solution, in which the solute as well as solvent are liquid?
- (1) C_6H_6 and $C_6H_5CH_3$; $\Delta_{sol}H > 0$; $\Delta_{sol}V = 0$
 - (2) $CH_3-\overset{\overset{O}{\parallel}}{C}-CH_3$ and $CHCl_3$; $\Delta_{sol}H < 0$; $\Delta_{sol}V < 0$
 - (3) H_2O and HCl ; $\Delta_{sol}H > 0$; $\Delta_{sol}V < 0$
 - (4) H_2O and CH_3OH ; $\Delta_{sol}H > 0$; $\Delta_{sol}V < 0$
10. Effect of adding a non-volatile solute to a solvent is:
- (1) to lower the vapour pressure
 - (2) to increase its freezing point
 - (3) to increase its boiling point
 - (4) to decrease its osmotic pressure
11. Which of the following forms is an ideal solution?
- (1) Ethyl bromide + Ethyl iodide
 - (2) Ethyl alcohol + Water
 - (3) Chloroform + Benzene
 - (4) Benzene + Toluene



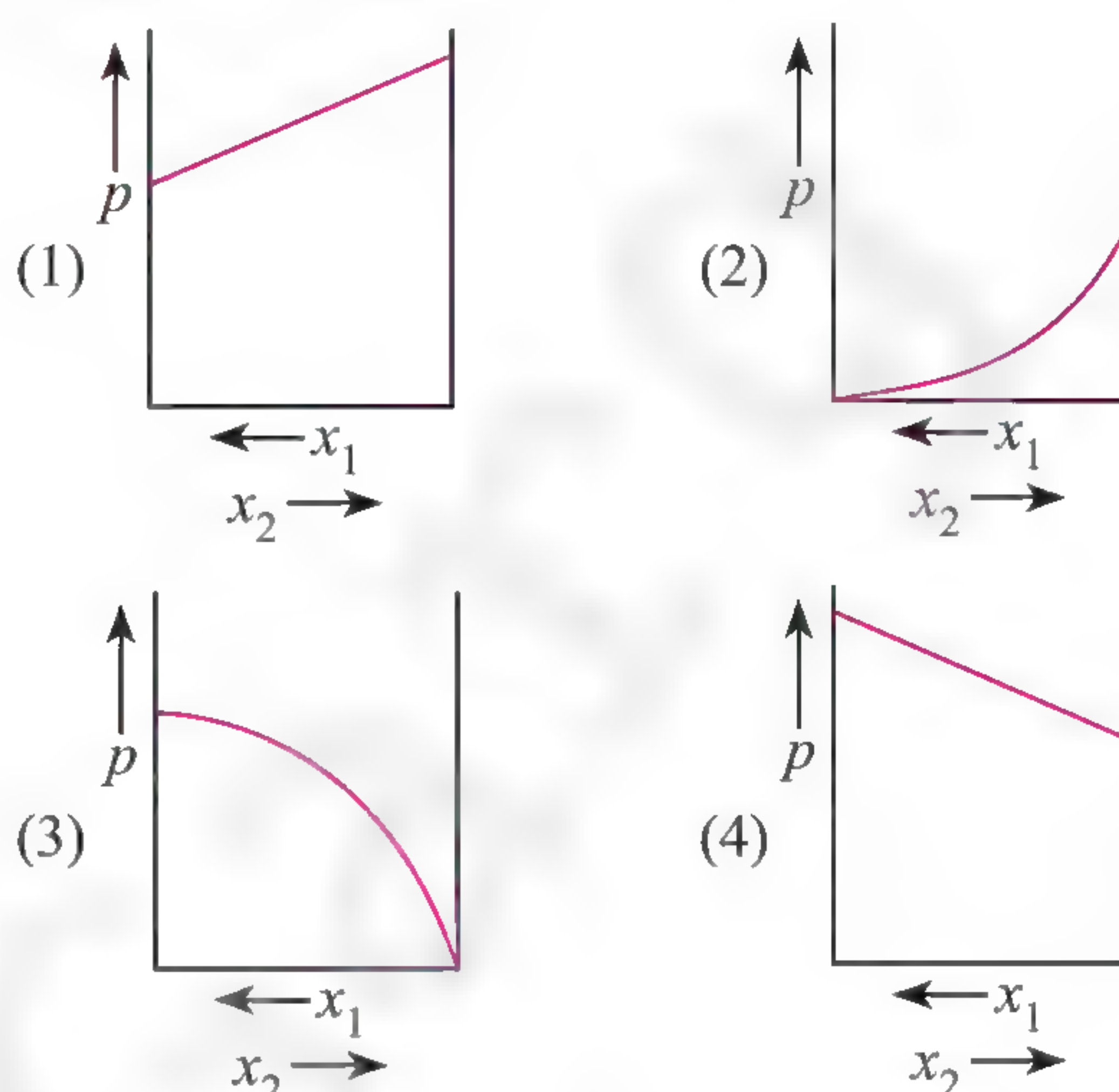
Choose the correct option:

- (1) A represents vapour composition and B represents liquid composition.
 - (2) A as well as B represent liquid composition.
 - (3) both A and B represent vapour composition.
 - (4) A represents liquid composition and B represents vapour composition.
13. When acetone and chloroform are mixed, hydrogen bonding takes place between them. Such a liquid pair will cause
- (1) Positive deviation from Raoult's law.
 - (2) Negative deviation from Raoult's law.
 - (3) No deviation from Raoult's law.
 - (4) Cannot be predicted.
14. A maxima or minima is obtained in the temperature. The composition curve of a mixture of two liquids does not indicate
- (1) That the liquids are immiscible with one another
 - (2) That the liquids are partially miscible at the maximum or minimum.

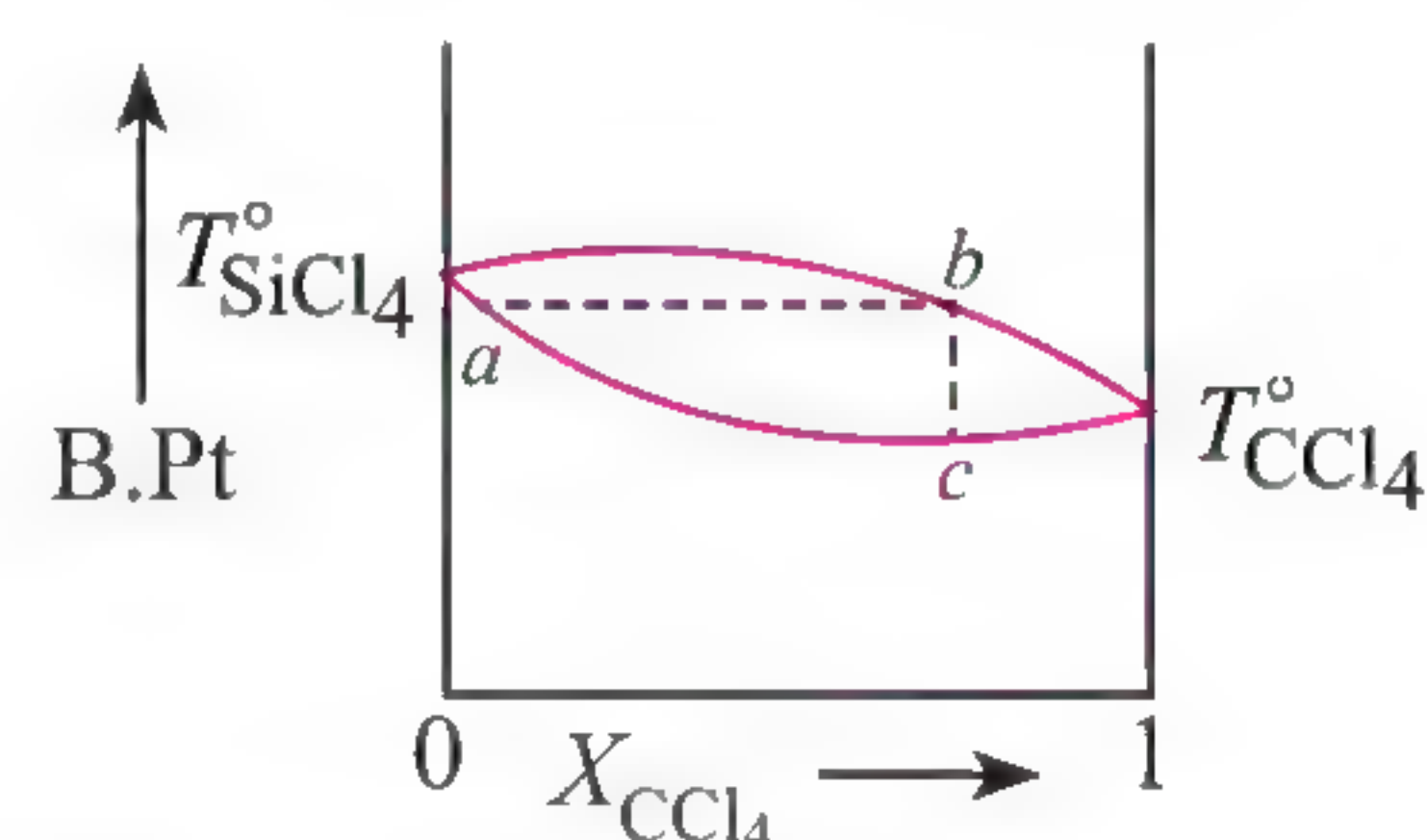
(3) An azeotropic mixture.

(4) A eutectic formation.

15. For a binary ideal liquid solution, the variation in total vapour pressure versus composition of solution is given by which of the curves?



16. The diagram given below depicts the boiling point as the function of composition of the mixture of CCl_4 and $SiCl_4$. Which of the following statements about the diagram is/are true?



- (1) The point a represents the composition of solution and the point b that of the vapour in equilibrium
 - (2) The proportion of CCl_4 in the solution is smaller than that in the vapour in equilibrium
 - (3) bc represents the condensation of the vapour
 - (4) The point c represents the composition of solution and the point b that of the vapour in equilibrium.
17. On mixing 1 mole of C_6H_6 ($P^0 = 42$ mm) and 2 mole of C_7H_8 ($P^0 = 36$ mm), one can conclude:
- (1) Total vapour pressure of mixture = 38 mm
 - (2) Mole fraction of vapours of C_6H_6 above liquid mixture $= \frac{7}{19}$
 - (3) Positive deviation from Raoult's law
 - (4) Both forms ideal solution
18. Composition of an azeotrope
- (1) Is independent of external pressure because it is a compound
 - (2) Alters on changing the external pressure as it is not a compound
 - (3) Remains unchanged during distillation at a constant external pressure
 - (4) Fluctuates even at constant pressure

19. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is (are):

- (1) ΔG is positive (2) ΔS_{system} is positive
 (3) $\Delta S_{\text{surroundings}} = 0$ (4) $\Delta H = 0$

20. Which of the following statements is/are wrong for a solution of chloroform and acetone?

- (1) The solution formed is an ideal solution
 (2) The solution formed is a non-ideal solution with positive deviation from Raoult's law
 (3) The solution formed is a non-ideal solution with negative deviation from Raoult's law
 (4) The solution behaves ideally or non-ideally depending upon its composition

Colligative Properties and Vant Hoff factor

21. Osmotic pressure of a solution is

- (1) Directly proportional to the molar concentration of the solution.
 (2) Inversely proportional to the molecular weight of the solute.
 (3) Inversely proportional to the temperature.
 (4) Directly proportional to the volume of the solution.

22. Which of the following is/are true?

- (1) For the same solution, elevation in boiling point = depression in freezing point.
 (2) The Van't Hoff factor for a dilute solution of BaCl_2 is 3.
 (3) The elevation in boiling point is due to increase in vapour pressure.
 (4) The depression in freezing point is due to decrease in vapour pressure.

23. To 10 mL of 1 M BaCl_2 solution 5 mL of 0.5 M K_2SO_4 is added. BaSO_4 is precipitated out. What will happen?

- (1) Freezing point will increase.
 (2) Boiling point will increase.
 (3) Freezing point will lower down.
 (4) Boiling point will lower down.

24. A difference between diffusion and osmosis is

- (1) A semi-permeable membrane is required for osmosis while diffusion requires no semi-permeable membrane.
 (2) In osmosis movement of molecules is only in one direction whereas in diffusion movement is on both sides.
 (3) In osmosis only the solvent moves while in diffusion both solute and solvent move.
 (4) None of these.

25. Which of the following statements is/are correct?

- (1) The freezing point of water is depressed by the addition of glucose.
 (2) The degree of dissociation of a weak electrolyte decrease as its concentration decreases.
 (3) Energy is released when a substance dissolves in water provided that the hydration energy of the substance is more than its lattice energy.

(4) If two liquids that form an ideal solution are mixed, the change in entropy is positive.

26. Consider the two solutions:

I: 0.5 M NaCl aqueous solution at 25°C;

NaCl is completely ionized.

II: 2.0 M $\text{C}_6\text{H}_5\text{COOH}$ in benzene at 25°C,

$\text{C}_6\text{H}_5\text{COOH}$ dimerizes to the full extent.

Which of the following statements(s) is(are) correct?

- (1) Both the solutions display equal osmotic pressure.
 (2) Both have equal vapour pressure.
 (3) Solution II is hypertonic.
 (4) Solution II has greater depression in freezing point than solution I.

27. Consider the following solutions:

I. 1 M sucrose

II. 1 M KCl

III. 1 M benzoic acid in benzene

IV. 1 M $(\text{NH}_4)_3\text{PO}_4$

Which of the following is/are true?

- (1) All solutions are isotonic.
 (2) III is hypotonic of I, II, and IV.
 (3) I, II, and III are hypertonic of IV.
 (4) IV is hypertonic of I, II, and III.

28. The osmotic pressure of a solution depends on

- (1) Nature of solute
 (2) Nature of solvent
 (3) Temperature
 (4) Molar concentration of solute

29. 1.2575 g sample of $[\text{Cr}(\text{NH}_3)_6]\text{SO}_4\text{Cl}$ ($M_w = 251.5$) is dissolved to prepare 250 mL solution showing an osmotic pressure of 1.478 atm of Hg at 27°C. Which of the following statements is/are correct about this solution?

- (1) Each molecule furnishes three ions in solution.
 (2) The Van't Hoff factor is = 3.
 (3) The equilibrium molarity of $[\text{Cr}(\text{NH}_3)_6]\text{SO}_4\text{Cl} = 0$.
 (4) The equilibrium molarity of $[\text{Cr}(\text{NH}_3)_6]^{3+} = 0.02$ M.

30. 2 L of 1 molar solution of a complex salt $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ($M_w = 266.5$) shows an osmotic pressure of 98.52 atm. The solution is now treated with 1 L of 6 M AgNO_3 , which of the following are correct?

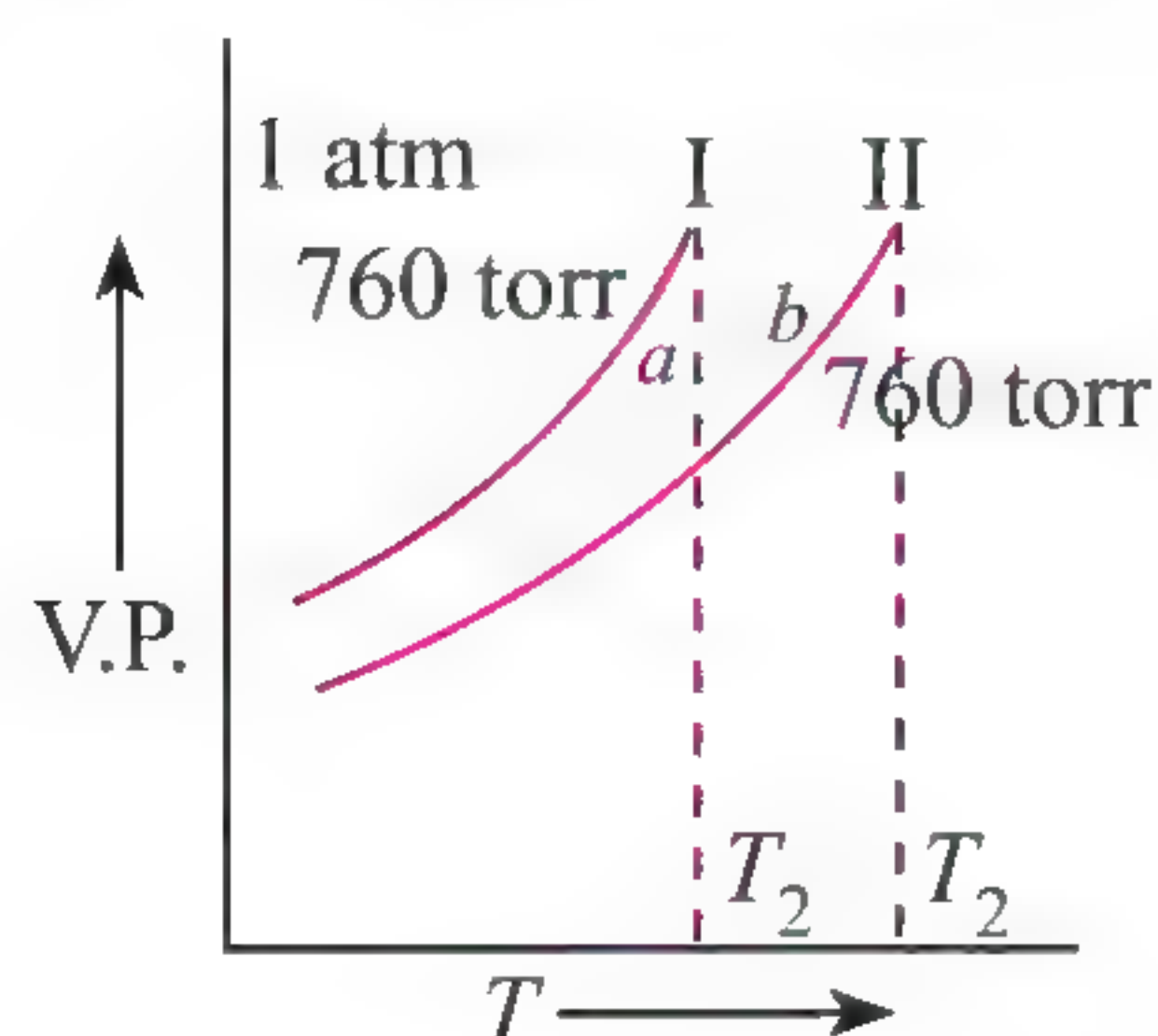
- (1) Weight of AgCl precipitated is 861 g.
 (2) The clear solution will show an osmotic pressure of 98.52 atm.
 (3) The clear solution will show an osmotic pressure of 65.68 atm.
 (4) 2 mol of $[\text{Cr}(\text{H}_2\text{O})_6] (\text{NO}_3)_3$ will be present in the solution.

31. For a given value of degree of dissociation, which of the following have correct Van't Hoff factor?

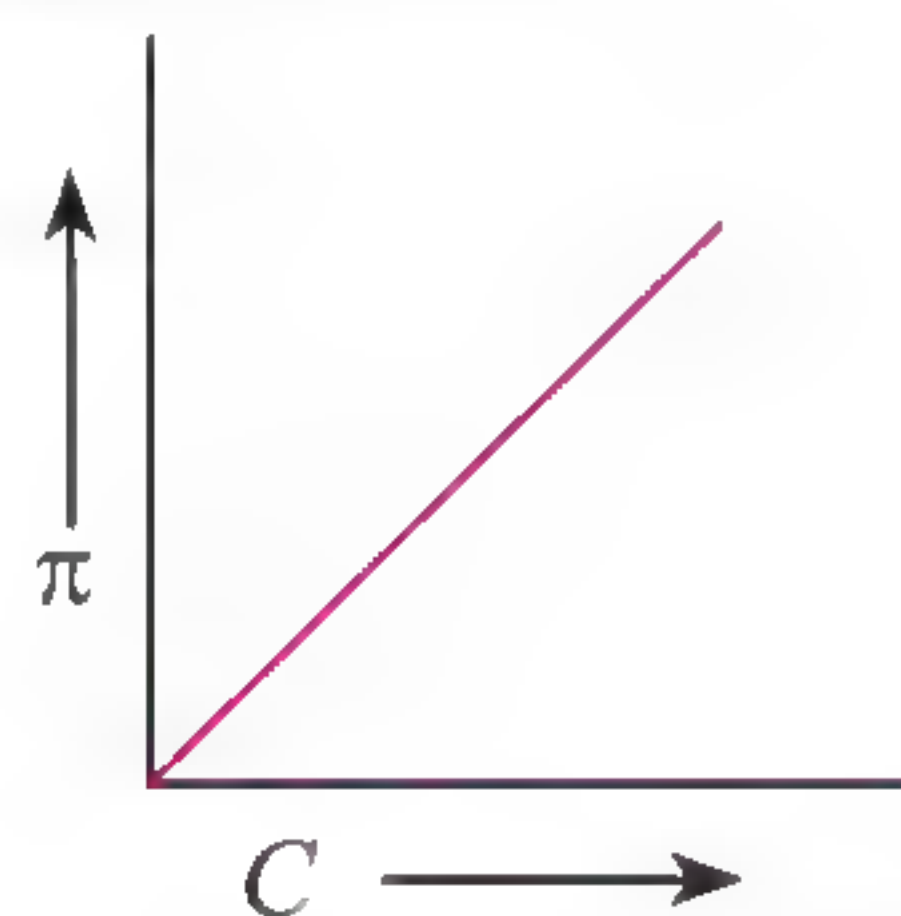
- (1) NaCl, $i = 2 + \alpha$

- (2) $\text{Ca}(\text{NO}_3)_2$, $i = 1 + 2\alpha$
 (3) $\text{K}_4[\text{Fe}(\text{CN})_6]$, $i = 1 + 4\alpha$
 (4) $(\text{NH}_4)_3\text{PO}_4$, $i = 3 + \alpha$

32. Vapour pressure–temperature curves of pure solvent and a solution containing a non-volatile solute are shown in the figure. Select the correct statement(s)



- (1) Curve I represents the variation of vapour pressure of solution and II that of solvent with temperature
 (2) Curve I and II represents the variation of vapour pressures of solvent and solution respectively with temperature
 (3) Gap ab represents $K_b m$ for the solution
 (4) Gap ab represents $K_f m$ for the solution
33. A graph showing variation of osmotic pressure (π) versus molar concentration (C) of an aqueous solution at temperature T is given below:



The slope of the line **doesn't** represent:

- (1) Solution constant R
 (2) Absolute temperature T
 (3) RT
 (4) Degree of ionization of solute?

Linked Comprehension Type

Paragraph 1

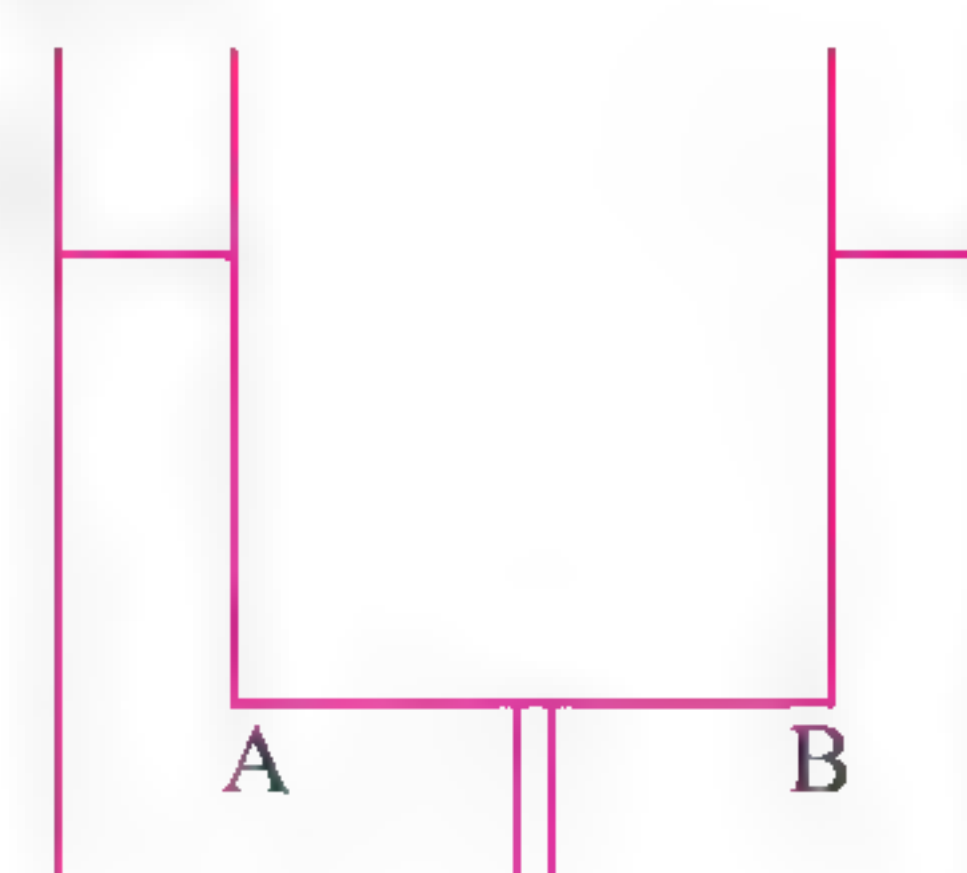
The osmotic pressure π depends on the molar concentration of the solution ($\pi = CRT$). If two solutions are of equal solute concentration and, hence, have the same osmotic pressure, they are said to be isotonic. If two solutions are of unequal osmotic pressures, the more concentrated solution is said to be hypertonic and the more diluted solution is described as hypotonic.

Osmosis is the major mechanism for transporting water upward in the plants. Answer the following questions:

1. A plant cell shrinks when it is kept in:
 (1) Hypotonic solution (2) Hypertonic solution
 (3) Isotonic solution (4) Pure water

2. What would be the percent strength of solution of urea that would be isotonic with 4.5% solution of glucose?
 (1) 4.5% (2) 13.5%
 (3) 1.5% (4) 9%
3. The glucose solution to be injected into the bloodstream and the blood itself should have the same
 (1) Molarity (2) Vapour pressure
 (3) Osmotic pressure (4) Viscosity
4. Isotonic solutions have same
 (1) Density (2) Molarity
 (3) Molality (4) Normality
 (5) Osmotic pressure
5. Osmotic rise of a solution depends on
 (1) Concentration (2) Temperature
 (3) Nature of solvent (4) All of these

Paragraph 2



Compartments A and B have the following combinations of solution:

A	B
1. 0.1 M KCl	0.2 M KCl
2. 0.1% (m/V) NaCl	10% (m/V) NaCl
3. 18 g L ⁻¹ glucose	34.2 g L ⁻¹ sucrose
4. 20% (m/V) glucose	10% (m/V) glucose

Answer the following questions:

6. Indicate the number of solutions which is/are isotonic.
 (1) 1 only (2) 3 only
 (3) 4 only (4) 2 only
7. The solutions in which compartment B is hypertonic.
 (1) 1, 2 (2) 2, 3
 (3) 3, 4 (4) 1, 4
8. Indicate the solution(s) in which compartment A will show an increase in volume.
 (1) 4 (2) 2
 (3) 3 (4) 5
9. Indicate the solution(s) in which compartment B will show an increase in volume.
 (1) 1, 2, 4 (2) 1, 2
 (3) 2, 3 (4) 3, 4
10. The solution in which there will be no change in the level of the solution in the compartments A and B is.
 (1) 1 (2) 2
 (3) 4 (4) 3

Paragraph 3

A solution M is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9

Given: Freezing point depression constant of water

$$(K_f^{\text{water}}) = 1.86 \text{ K kg mol}^{-1}$$

Freezing point depression constant of ethanol

$$(K_f^{\text{ethanol}}) = 2.0 \text{ K kg mol}^{-1}$$

Boiling point elevation constant of water

$$(K_b^{\text{water}}) = 0.52 \text{ K kg mol}^{-1}$$

Boiling point elevation constant of ethanol

$$(K_b^{\text{ethanol}}) = 1.2 \text{ K kg mol}^{-1}$$

Standard freezing point of water = 273 K

Standard freezing point of ethanol = 155.7 K

Standard boiling point of water = 373 K

Standard boiling point of ethanol = 351.5 K

Vapour pressure of pure water = 32.8 mm Hg

Vapour pressure of pure ethanol = 40 mm Hg

Molecular weight of water = 18 g mol⁻¹

Molecular weight of ethanol = 46 g mol⁻¹

In answering the following questions consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative.

11. The freezing point of the solution M is

- (1) 268.7 K (2) 268.5 K
(3) 150.9 K (4) 268.7 K

12. The vapour pressure of the solution M is

- (1) 39.3 mm Hg (2) 36.0 mm Hg
(3) 29.5 mm Hg (4) 28.8 mm Hg

13. Water is added to the solution M such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is

- (1) 380.4 K (2) 376.2 K
(3) 375.5 K (4) 354.7 K

Paragraph 4

A certain vessel X has water and nitrogen gas at a total pressure of 2 atm and 300 K. All the contents of vessel are transferred to another vessel Y having half the capacity of the vessel X. The pressure of N₂ in this vessel was 3.8 atm at 300 K. The vessel Y is heated to 320 K and the total pressure observed was 4.32 atm. Assume that the volume occupied by the gasses in vessel is equal to the volume of the vessel. Calculate the following:

14. Pressure of H₂O(g) in X at 320 K.

- (1) 0.1 (2) 0.2
(3) 1.0 (4) 2.0

15. Pressure of N₂ at 320 K.

- (1) 4.0 (2) 4.05
(3) 5.05 (4) 1.05

16. Pressure of water vapour at 320 K

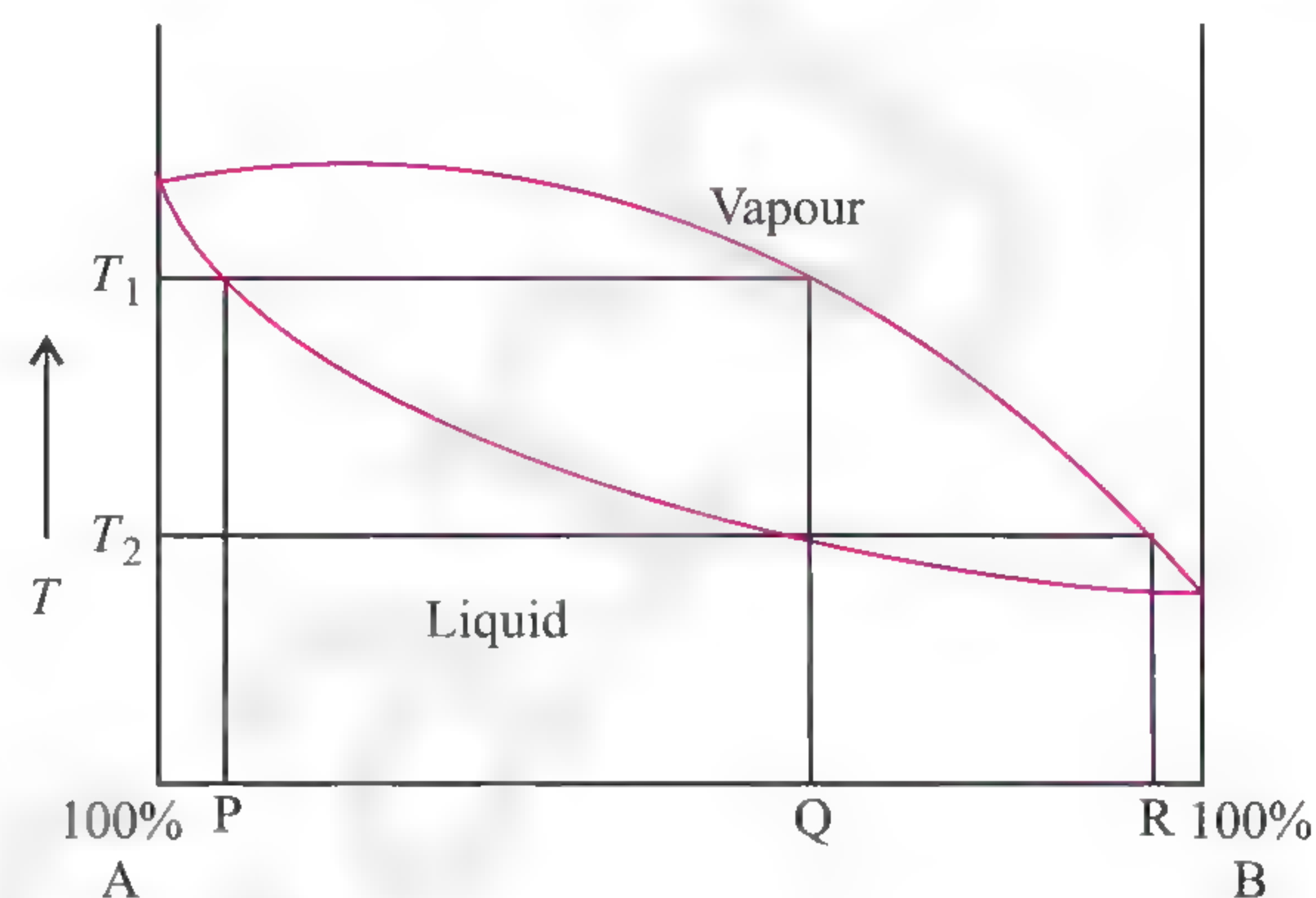
- (1) 0.27 (2) 0.32
(3) 4.0 (4) 1.0

17. Enthalpy of vapourization.

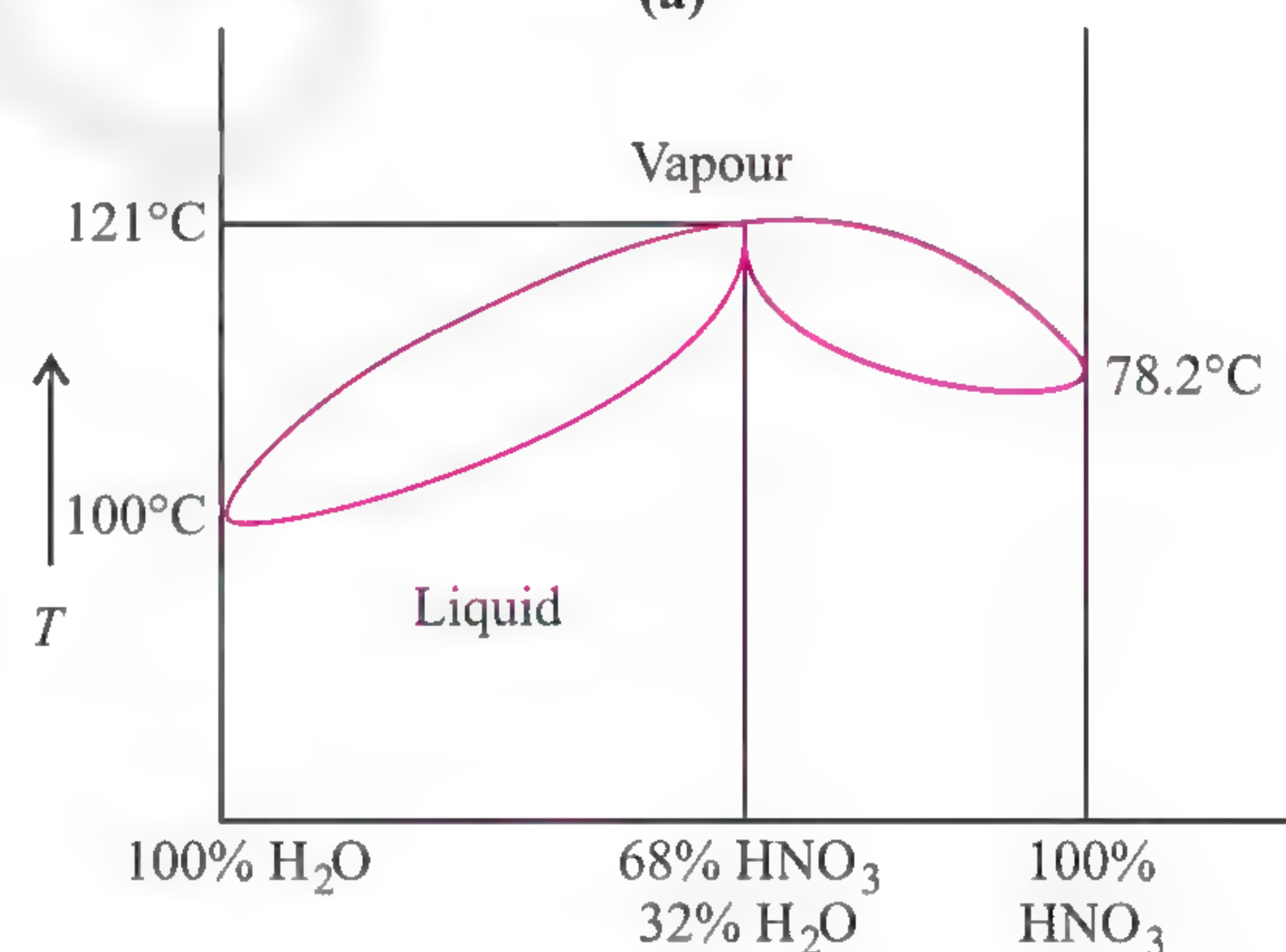
- (1) 30.00 (2) 35.65
(3) 38.65 (4) 39.65

Paragraph 5

Figure (a) represents the distillation of mixture of liquid A and liquid B which gives both of pure liquid A and B. While Fig. (b) represents the azeotropic mixture of HNO₃ and H₂O which distillation gives an azeotropic mixture and either of pure liquid. We cannot separate both the pure liquid, i.e., H₂O and HNO₃.



(a)



(b)

18. What is the result of distilling a mixture of 50% HNO₃ and 50% H₂O?

- (1) Pure water and azeotropic mixture can be separated.
(2) Pure H₂O and pure HNO₃ can be separated.
(3) Pure HNO₃ and azeotropic mixture can be separated.
(4) None of these

19. What is the result of distilling a mixture of 80% HNO₃ and 20% H₂O?

- (1) Pure H₂O and azeotropic mixture can be separated.
(2) Pure H₂O and pure HNO₃ can be separated.
(3) Pure HNO₃ and azeotropic mixture can be separated.
(4) None of these

20. Which of the following statements is/are correct?

- i. HNO₃ solution is not obeying the Raoult's law.
ii. More the difference in vapour pressure of pure compounds forming a mixture, easier to separate them through distillation.
iii. In Fig. (a), T₂ is less than T₁ because the liquid of composition Q is richer in more volatile component.

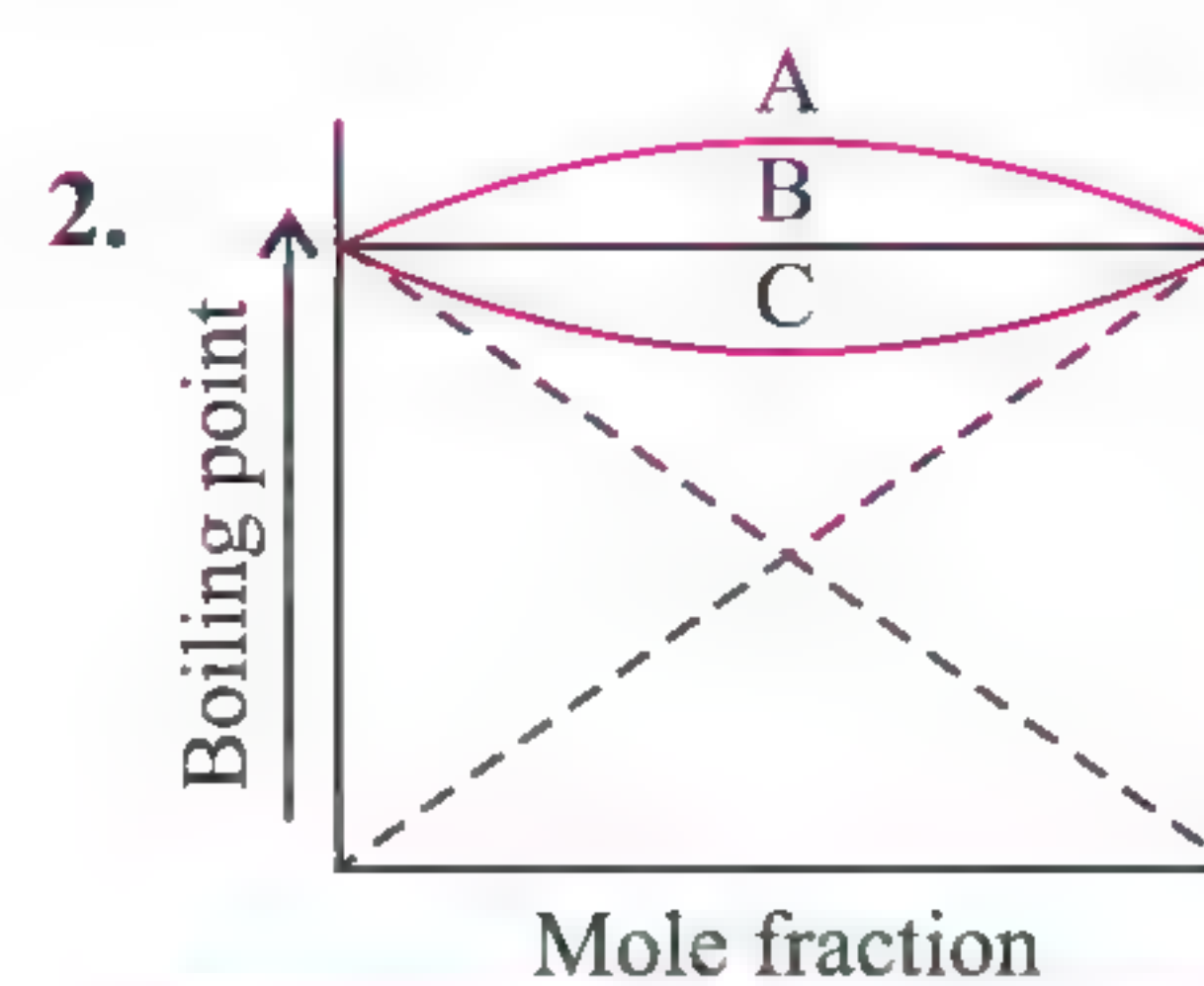
- (1) (ii) and (iii) (2) (ii)
(3) (i) and (ii) (4) (i), (ii) and (iii)

21. In Fig. (a), a solution of 50% of A and 50% of B on distillation results into

- (1) Separation of an azeotropic mixture and pure A.
- (2) Separation of an azeotropic mixture and pure B.
- (3) Separation of both pure A and pure B.
- (4) None of these

22. At temperature T_1 and composition Q , which of the following is true?

- (1) Vapour phase is richer in B while liquid phase is richer in A.
- (2) Distillation of composition Q gives only pure A.
- (3) Distillation of composition Q gives pure A and pure B.
- (4) Distillation of composition Q gives higher percentage of B than A.



	Column I		Column II
a.	A	p.	(+) deviation
b.	B	q.	Ideal
c.	C	r.	(-) deviation

3. Match the following:

	Column I		Column II
a.	Urea, glucose, fructose	p.	1:0.8:1
b.	NaCl, MgCl ₂ , K ₂ SO ₄	q.	1:2:3
c.	Al ₂ (SO ₄) ₃ , Na ₃ PO ₄ , K ₄ [Fe(CN) ₆]	r.	1:1:1
d.	Glucose, NaCl, CaCl ₂	s.	2:3:3

4.

	Column I		Column II
a.	Hypertonic	p.	Solutions having same osmotic pressure
b.	Isotonic	q.	One solution has higher osmotic pressure than the second solution.
c.	Van't Hoff	r.	Theory of dilute solution
d.	Beckmann	s.	Differential thermometer

5.

	Column I		Column II
a.	$P^\circ - P_s$	p.	$\frac{\text{Observed colligative property}}{\text{Normal colligative property}}$
b.	$P^\circ \times \chi_A = P_A$	q.	Lowering in vapour pressure
c.	Mixture that boils like pure solvent	r.	Azeotropic mixture
d.	Van't Hoff factor	s.	Raoult's law

Matrix Match Type

This section contains questions each with two columns—I and II. Match the items given in column I with that in column II.

1. p_A = partial pressure of component A in liquid mixture, P_A° = vapour pressure of A, χ_A = mole fraction of A in liquid mixture

	Column I		Column II
a.	C ₂ H ₅ OH + H ₂ O	p.	Azeotropic mixture
b.	C ₂ H ₅ Br + C ₂ H ₅ I	q.	Obeys Raoult's law
c.	$p_A = \chi_A P_A^\circ$	r.	Non-ideal solution with positive deviation
d.	H ₂ O + H ₂ SO ₄	s.	Non-ideal solution with negative deviation
		t.	Ideal solution

6.

	Compounds		Characteristics (I)		Characteristics (II)
a	Brass	i	Interstitial solid solution	p	Formed by placing atoms of one kind into the place of other substance in its crystal lattice
b	Tungsten carbide	ii	Substitutional solid solution	q	Formed by placing atoms of one kind into the voids in the lattice of atoms of other substance
c	Na ₂ CO ₃ ·H ₂ O	iii	Solubility does not increase or decrease continuously	r	Hydration energy is less than lattice energy
d	NaNO ₃	iv	Solubility decreases continuously with increase of temperature	s	On heating change at a particular temperature from one polymorphic form to another
e	CaCl ₂ ·6H ₂ O	v	Solubility increases continuously with increase of temperature	t	Process of dissolution is endothermic

7.

	Gases		Characteristics (I)		Characteristics (II)
a	O ₂ and N ₂	i	More soluble in H ₂ O	p	Lower K _H (Henry's constant) value at a given pressure
b	SO ₂ and NH ₃	ii	Less soluble in H ₂ O	q	Higher K _H value at a given pressure
c	Helium and Ar	iii	Sparingly soluble in acetone. Solubility increases slightly with increase of temperature	r	K _H value increases with increase of temperature
d	Partial pressure of a gas is related	iv	Solubility of gases decreases with increase of temperature	s	Chemically react with water
		v	Mole fraction of the dissolved gas	t	K _H

Numerical Value Type

- 12.2 g of benzoic acid ($M_w = 122$) in 100 g water has elevation in boiling point of 0.27. $K_b = 0.54 \text{ K kg mol}^{-1}$. If there is 100% polymerization, the number of molecules of benzoic acid in associated state is
(1) 2 (2) 1 (3) 3 (4) 4
- The ratio of the value of any colligative property for BaCl₂ solution of urea solution under similar condition is
(1) 2 (2) 3 (3) 1 (4) 4
- The Van't Hoff factor for a solute which does not dissociate or associate in solution is
(1) 0 (2) 2 (3) 3 (4) 1
- Compound PdCl₄·6H₂O is a hydrated complex; 1 m aqueous solution of it has freezing point 269.28 K. Assuming 100% ionization of complex, calculate the number of ions furnished by complex in the solution.
(1) 1 (2) 2 (3) 4 (4) 0
- The total number of colligative properties are
(1) 1 (2) 2 (3) 3 (4) 4
- If for a sucrose, elevation in boiling point is 1.0°C, then what will be the boiling point of NaCl solution for same molal concentration?
(1) 1.0°C (2) 2.0°C (3) 3.0°C (4) 4.0°C
- The osmotic pressure of urea solution at 10°C is 200 mm. becomes 105.3 mm when it is diluted and temperature raised to 25°C. The extent of dilution is
(1) 8 times (2) 5 times (3) 4 times (4) 2 times
- The osmotic pressure of a solution containing 40 g of solute (molecular mass 246) per litre at 27°C is ($R = 0.0822 \text{ atm L mol}^{-1}$)
(1) 3.0 atm (2) 4.0 atm (3) 2.0 atm (4) 1.0 atm

Archives

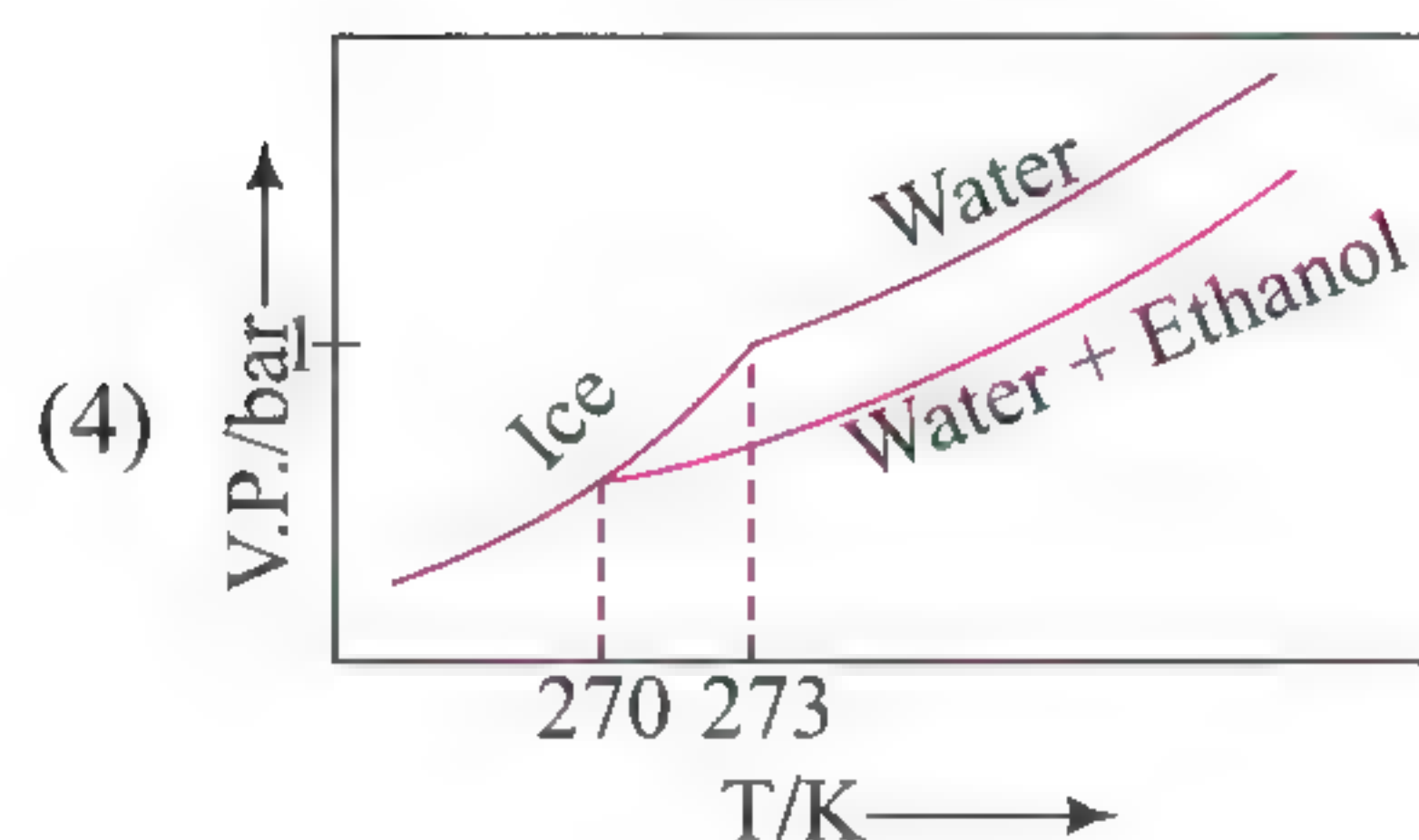
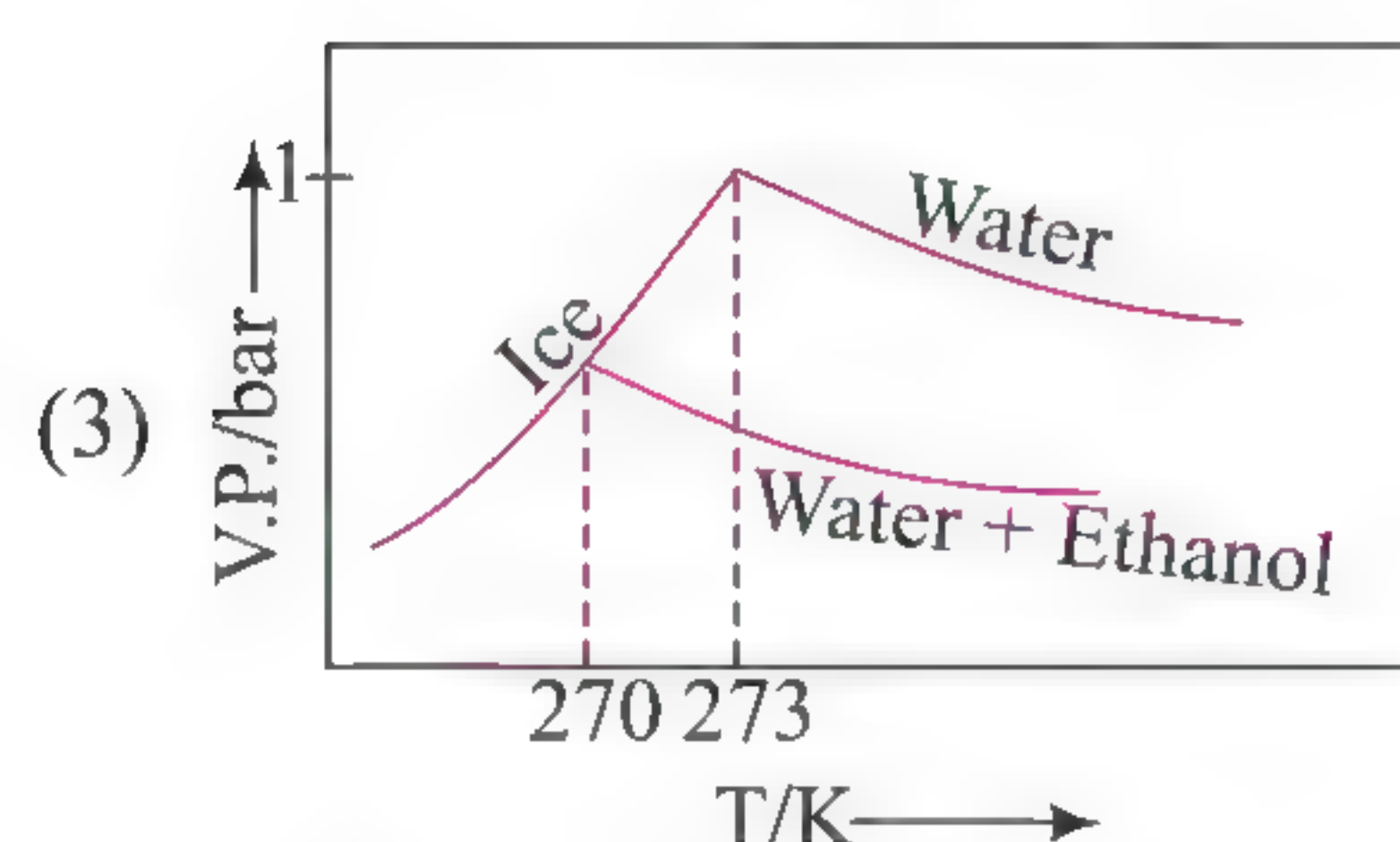
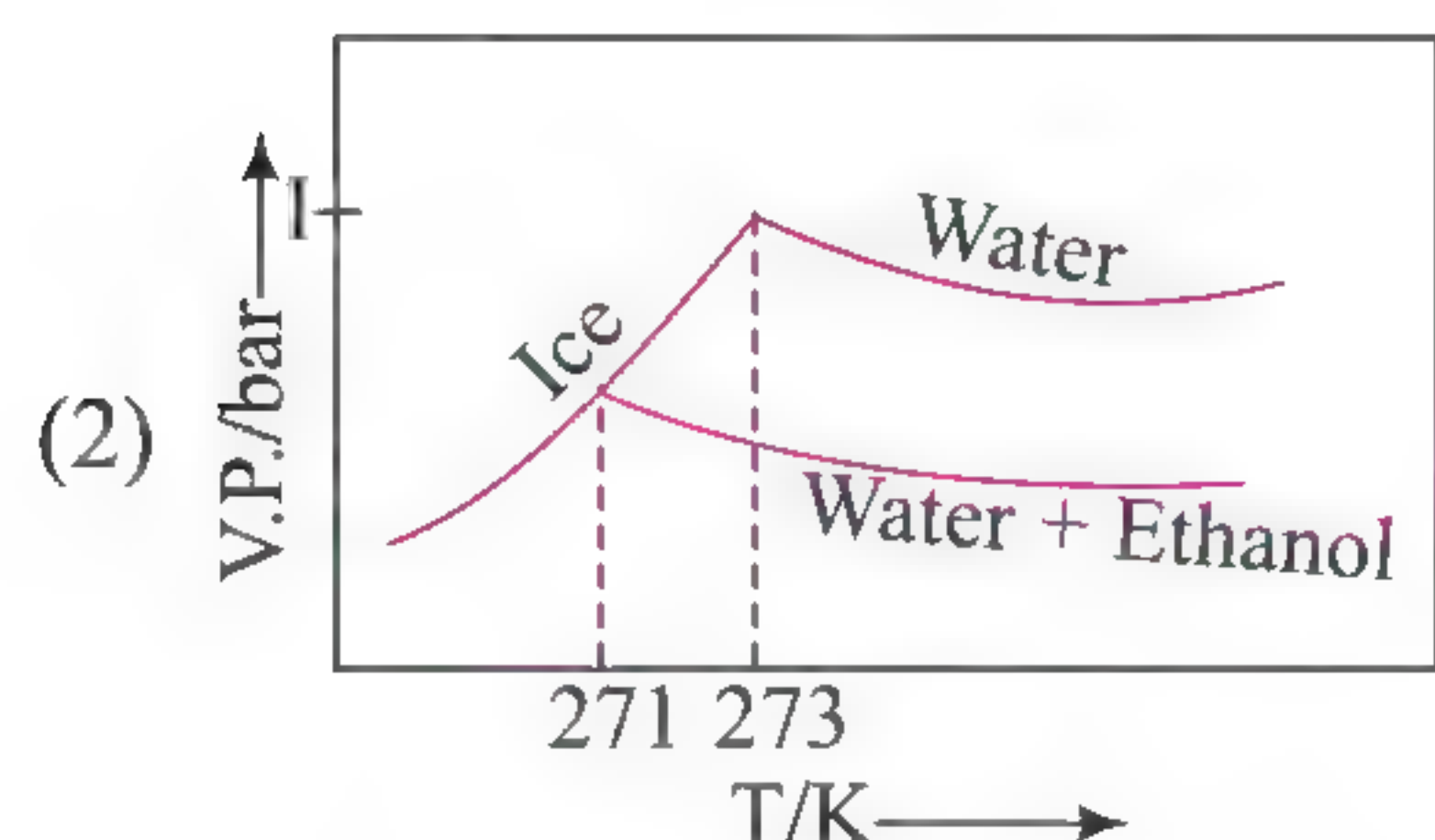
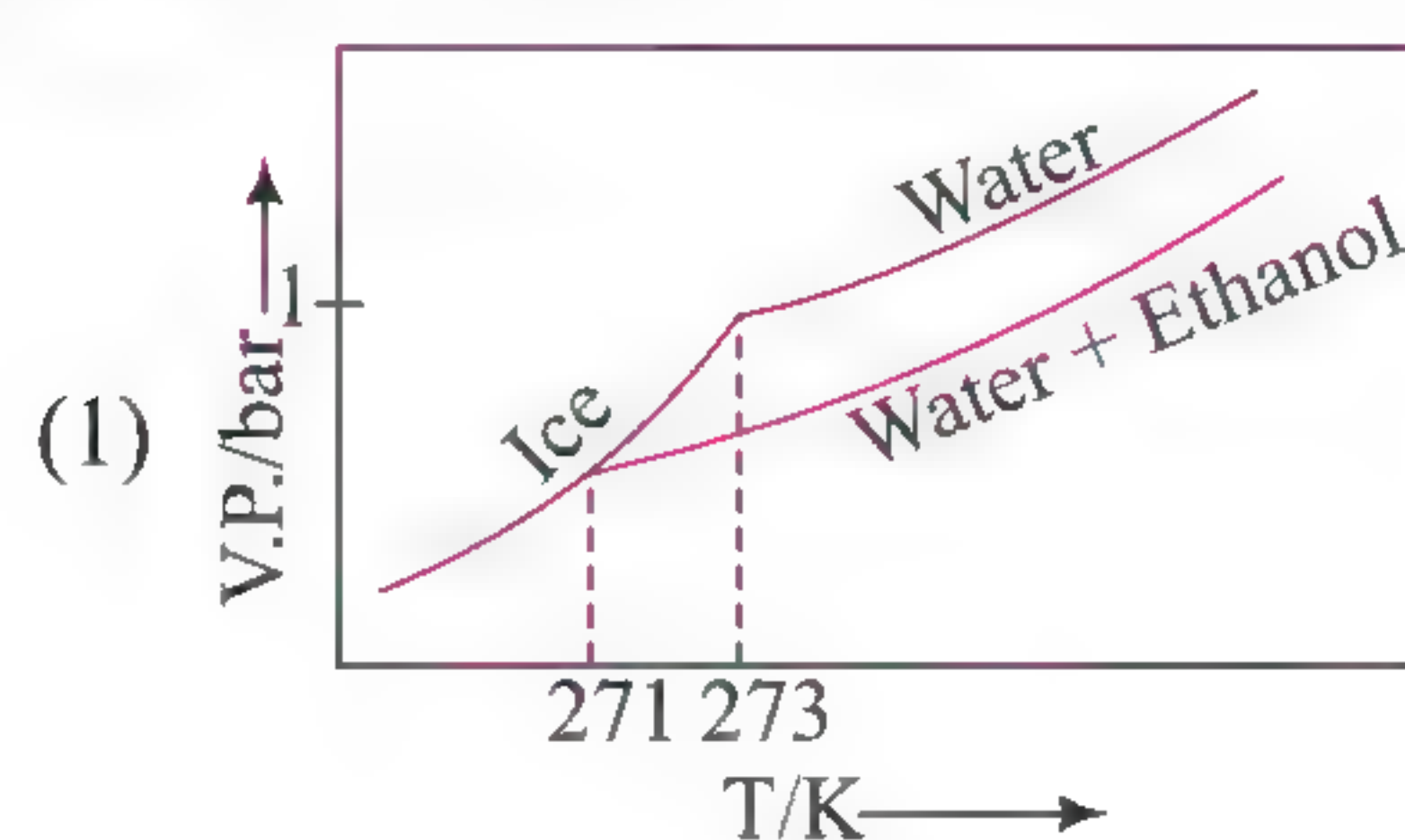
JEE ADVANCED

Single Correct Answer Type

- Henry's law constant for the solubility of nitrogen gas in water at 298 K is $1.0 \times 10^{-5} \text{ atm}$. The mole fraction of nitrogen in air is 0.8. The number of moles of nitrogen from air dissolved in 10 mol of water at 298 K and 5 atm pressure is
(1) $4.0 \times 10^{-4} \text{ atm}$ (2) $4.0 \times 10^{-5} \text{ atm}$
(3) $5.0 \times 10^{-4} \text{ atm}$ (4) $4.0 \times 10^{-6} \text{ atm}$
(IIT-JEE 2009)
- The freezing point (°C) of a solution containing 0.1 g of K₃[Fe(CN)₆] (molecular weight 329) in 100 g of water ($K_f = 1.86 \text{ K kg mol}^{-1}$).
(1) 2.3×10^{-2} (2) 5.7×10^{-2}
(3) 5.7×10^{-3} (4) -1.20×10^{-2}
(IIT-JEE 2011)
- For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is 2°C. Assuming concentration of

solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is (take $K_b = 0.76 \text{ K kg mol}^{-1}$)

- (1) 724 (2) 740 (3) 736 (4) 718
(IIT-JEE 2012)
- The vapour pressure of acetone at 20°C is 185 torr. When 1.2 g of a non-volatile substance was dissolved in 100 g of acetone at 20°C, its vapour pressure was 183 torr. The molar mass (g mol⁻¹) of the substance is:
(1) 32 (2) 64 (3) 128 (4) 488
(JEE Advanced 2015)
- Pure water freezes at 273 K and 1 bar. The addition of 34.5 g of ethanol to 500 g of water changes the freezing point of the solution. Use the freezing point depression constant of water as 2 K kg mol^{-1} . The figure shown below represents plots of vapour pressure (V.P.) versus temperature (T). [Molecular weight of ethanol is 46 g mol^{-1}]
Among the following, the option representing change in the freezing point is -



(JEE Advanced 2017)

Multiple Correct Answers Type

1. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is(are)

- (1) ΔG is positive (2) ΔS_{system} is positive
(3) $\Delta S_{\text{surrounding}} = 0$ (4) $\Delta H = 0$

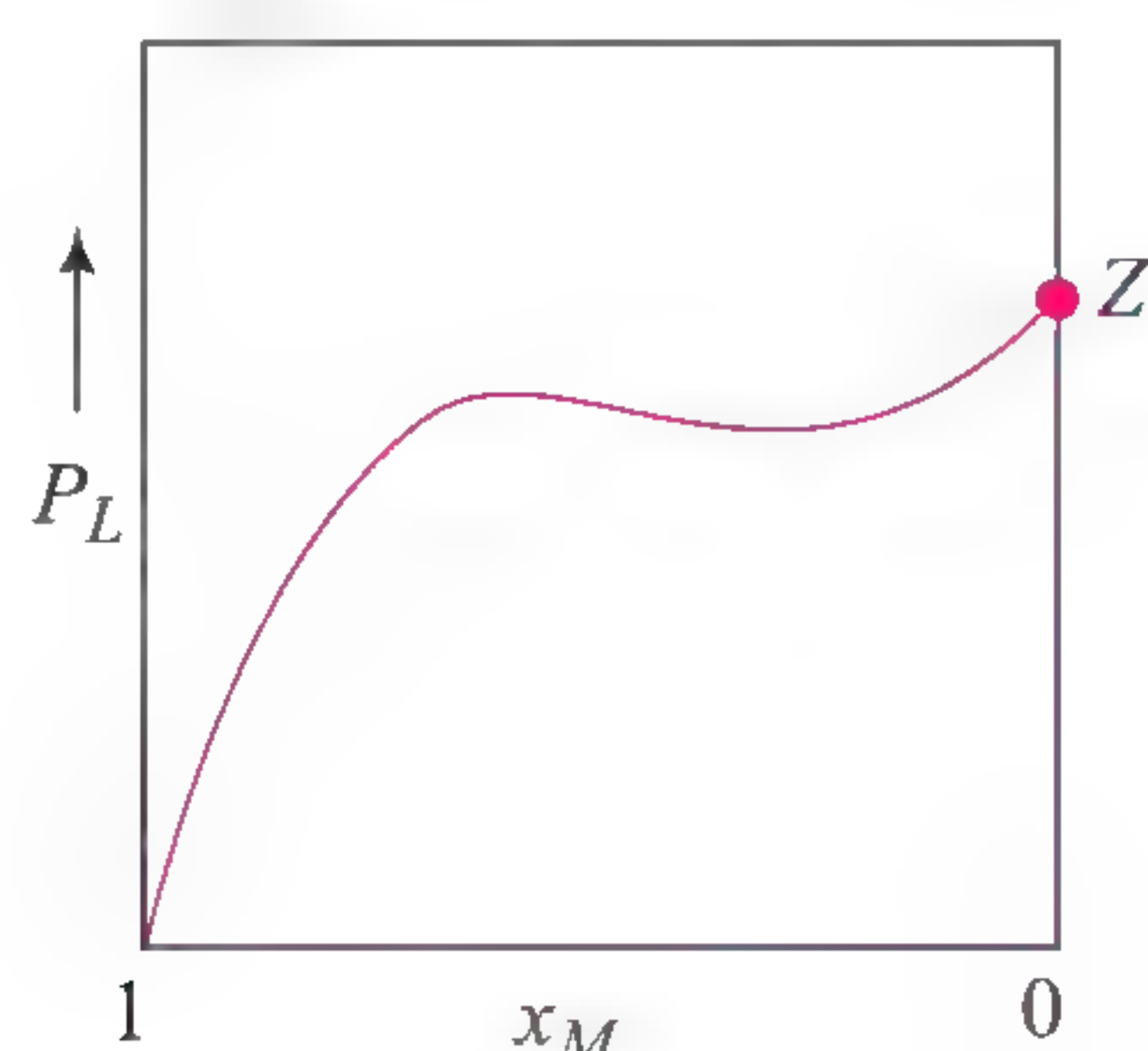
(JEE Advanced 2013)

2. Mixture(s) showing positive deviation from Raoult's law at 35°C is (are)

- (1) carbon tetrachloride + methanol
(2) carbon disulphide + acetone
(3) benzene + toluene
(4) phenol + aniline

(JEE Advanced 2016)

3. For a solution formed by mixing liquids L and M , the vapour pressure of L plotted against the mole fraction of M in solution is shown in the following figure. Here x_L and x_M represent mole fractions of L and M , respectively, in the solution. The correct statement(s) applicable to this system is (are)



- (1) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed from $x_L = 0$ to $x_L = 1$
(2) Attractive intermolecular interactions between $L-L$ in pure liquid L and $M-M$ in pure liquid M are stronger than those between $L-M$ when mixed in solution
(3) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed when $x_L \rightarrow 0$
(4) The point Z represents vapour pressure of pure liquid L and Raoult's law is obeyed when $x_L \rightarrow 1$

(JEE Advanced 2017)

Numerical Value Type

1. MX_2 dissociates into M^{2+} and X^\ominus ion in an aqueous solution, with a degree of dissociation (α) of 0.5. The ratio of the observed depression of freezing point of the aqueous solution to the value of the depression of freezing point in absence of ionic dissociation is

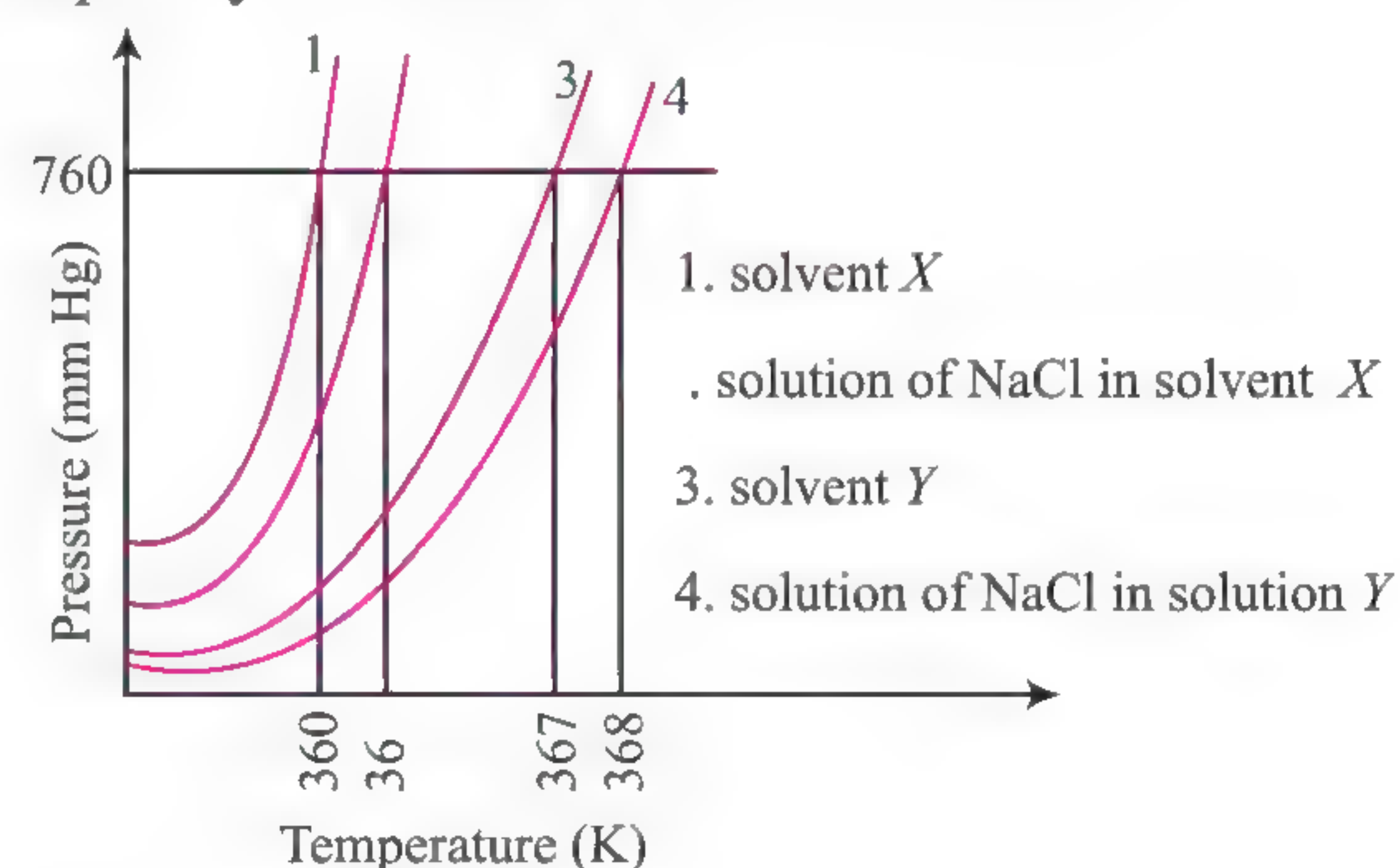
(JEE Advanced, 2014)

2. Liquids A and B form ideal solution over the entire range of composition. At temperature T , equimolar binary solution of liquids A and B has vapour pressure 45 Torr. At the same temperature, a new solution of A and B having mole fractions x_A and x_B , respectively, has vapour pressure of 22.5 Torr. value of x_A/x_B in the new solution is _____.

(given that the vapour pressure of pure liquid A is 20 Torr at temperature T)

(JEE Advanced 2018)

3. The plot given below shows $P-T$ curves (where P is the pressure and T is the temperature) for two solvents X and Y and isomolal solutions of NaCl in these solvents. NaCl completely dissociates in both the solvents.



On addition of equal number of moles of a non-volatile solute S in equal amount (in kg) of these solvents, the elevation of boiling point of solvent X is three times that of solvent Y . Solute S is known to undergo dimerization in these solvents. If the degree of dimerization is 0.7 in solvent Y , the degree of dimerization in solvent X is _____.

(JEE Advanced 2018)

4. On dissolving 0.5 g of a non-volatile non-ionic solute to 39 g of benzene, its vapour pressure decreases from 650 mm Hg to 640 mm Hg. The depression of freezing point of benzene (in K) upon addition of the solute is _____. (Given data: Molar mass and the molal freezing point depression constant of benzene are 78 g mol^{-1} and $5.12 \text{ K kg mol}^{-1}$, respectively)

(JEE Advanced 2019)

5. Liquid A and B form ideal solution for all compositions of A and B at 25°C . Two such solutions with 0.25 and 0.50 mole fractions of A have the total vapor pressures of 0.3 and 0.4 bar, respectively. What is the vapor pressure of pure liquid B in bar?

(JEE Advanced 2020)

Paragraph for Questions 6 and 7:

The boiling point of water in a 0.1 molal silver nitrate solution (solution A) is $x^\circ\text{C}$. To this solution A, an equal volume of 0.1 molal aqueous barium chloride solution is added to make a new

solution B. The difference in the boiling points of water in the two solutions A and B is $y \times 10^{-2}^\circ\text{C}$.

(Assume: Densities of the solutions A and B are the same as that of water and the soluble salts dissociate completely.

Use: Molal elevation constant (Ebullioscopic Constant), $K_b = 0.5 \text{ kg mol}^{-1}$; Boiling point of pure water as 100°C .)

6. The value of x is _____.

7. The value of $|y|$ is _____.

(JEE Advanced 2021)

Answers Key

EXERCISES**Single Correct Answer Type**

- | | | | | |
|----------|----------|----------|----------|----------|
| 1. (2) | 2. (2) | 3. (2) | 4. (2) | 5. (2) |
| 6. (1) | 7. (2) | 8. (1) | 9. (1) | 10. (1) |
| 11. (2) | 12. (3) | 13. (1) | 14. (1) | 15. (1) |
| 16. (2) | 17. (2) | 18. (1) | 19. (2) | 20. (2) |
| 21. (1) | 22. (1) | 23. (4) | 24. (3) | 25. (1) |
| 26. (4) | 27. (3) | 28. (3) | 29. (1) | 30. (2) |
| 31. (2) | 32. (1) | 33. (2) | 34. (4) | 35. (2) |
| 36. (2) | 37. (4) | 38. (2) | 39. (1) | 40. (1) |
| 41. (1) | 42. (1) | 43. (3) | 44. (4) | 45. (1) |
| 46. (1) | 47. (3) | 48. (2) | 49. (2) | 50. (3) |
| 51. (2) | 52. (1) | 53. (4) | 54. (4) | 55. (3) |
| 56. (4) | 57. (2) | 58. (4) | 59. (2) | 60. (3) |
| 61. (4) | 62. (4) | 63. (3) | 64. (3) | 65. (2) |
| 66. (3) | 67. (4) | 68. (4) | 69. (3) | 70. (3) |
| 71. (2) | 72. (3) | 73. (3) | 74. (2) | 75. (1) |
| 76. (2) | 77. (2) | 78. (4) | 79. (1) | 80. (1) |
| 81. (3) | 82. (4) | 83. (4) | 84. (1) | 85. (1) |
| 86. (1) | 87. (1) | 88. (3) | 89. (4) | 90. (4) |
| 91. (3) | 92. (2) | 93. (4) | 94. (2) | 95. (1) |
| 96. (1) | 97. (1) | 98. (2) | 99. (2) | 100. (1) |
| 101. (1) | 102. (2) | 103. (3) | 104. (3) | 105. (4) |
| 106. (1) | 107. (2) | 108. (4) | 109. (3) | 110. (3) |
| 111. (3) | 112. (1) | 113. (1) | 114. (1) | 115. (2) |
| 116. (1) | 117. (4) | 118. (1) | 119. (3) | 120. (3) |
| 121. (1) | 122. (4) | 123. (3) | 124. (3) | 125. (2) |
| 126. (1) | 127. (1) | 128. (4) | 129. (3) | 130. (1) |
| 131. (1) | 132. (2) | 133. (2) | 134. (2) | 135. (4) |
| 136. (3) | 137. (4) | 138. (3) | 139. (4) | 140. (3) |
| 141. (1) | 142. (2) | 143. (1) | 144. (3) | 145. (4) |
| 146. (2) | 147. (1) | 148. (1) | 149. (4) | 150. (4) |
| 151. (2) | 152. (2) | 153. (3) | 154. (1) | 155. (4) |
| 156. (1) | 157. (4) | 158. (1) | 159. (1) | 160. (4) |
| 161. (4) | 162. (1) | 163. (2) | 164. (4) | 165. (2) |
| 166. (1) | 167. (2) | 168. (1) | 169. (1) | 170. (1) |

Multiple Correct Answers Type

- | | | |
|-----------------|---------------|---------------|
| 1. (1, 2) | 2. (1, 2, 4) | 3. (1, 3, 4) |
| 4. (1, 2, 3, 4) | 5. (1, 3) | 6. (1, 2) |
| 7. (2, 4) | 8. (1, 2) | 9. (2, 4) |
| 10. (1, 3) | 11. (1, 4) | 12. (1, 2, 3) |
| 13. (3) | 14. (1, 3, 4) | 15. (1, 4) |

- | | | |
|---------------|------------------|---------------|
| 16. (1, 2, 3) | 17. (1, 2, 4) | 18. (2, 3) |
| 19. (2, 3, 4) | 20. (1, 2, 4) | 21. (1, 2) |
| 22. (2, 4) | 23. (2, 3) | 24. (1, 2, 3) |
| 25. (1, 3, 4) | 26. (1, 4) | 27. (2, 3, 4) |
| 28. (3, 4) | 29. (1, 2, 3, 4) | 30. (1, 3, 4) |
| 31. (2, 3) | 32. (2, 3) | 33. (1, 2, 3) |

Linked Comprehension Type

- | | | | | |
|---------|---------------|---------|----------|----------|
| 1. (3) | 2. (3) | 3. (3) | 4. (2,5) | 5. (1,2) |
| 6. (2) | 7. (1) | 8. (1) | 9. (2) | 10. (4) |
| 11. (3) | 12. (2) | 13. (2) | 14. (1) | 15. (2) |
| 16. (1) | 17. (4) | 18. (1) | 19. (3) | 20. (4) |
| 21. (3) | 22. (1, 3, 4) | | | |

Matrix Match Type

Q.No.	a	b	c	d	e
1.	p, r	q, t	q, t	p, s	—
2.	p	q	r	—	—
3.	r	s	p	q	—
4.	p	q	r	s	—
5.	q	s	r	p	—
6.	ii, p	i, q	iv, r	v, t	iii, s
7.	ii, iv, q, r	i, iv, p, s	iii, q	v, t	

Numerical Value Type

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (1) | 2. (2) | 3. (4) | 4. (2) | 5. (4) |
| 6. (4) | 7. (4) | 8. (2) | | |

ARCHIVES**JEE Advanced****Single Correct Answer Type**

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (1) | 2. (1) | 3. (1) | 4. (2) | 5. (4) |
|--------|--------|--------|--------|--------|

Multiple Correct Answers Type

- | | | |
|--------------|-----------|-----------|
| 1. (2, 3, 4) | 2. (1, 2) | 3. (2, 4) |
|--------------|-----------|-----------|

Numerical Value Type

- | | | | |
|-----------|------------|-----------|-----------|
| 1. (2) | 2. (19) | 3. (0.05) | 4. (1.02) |
| 5. (0.20) | 6. (100.1) | 7. (2.5) | |

Chapter 2

Concept Application Exercises

Exercise 2.1

1. a. Calculation of total vapour pressure

According to Raoult's law

Vapour pressure of a component

$$= \text{Vapour pressure of pure liquid} \times \text{Mole fraction}$$

Mole fraction of toluene, $\chi_{\text{toluene}} = 0.60$

Vapour pressure of pure toluene,

$$P_{\text{toluene}}^{\circ} = 0.0900 \text{ bar}$$

Partial vapour pressure of toluene,

$$P_{\text{toluene}} = 0.0900 \times 0.60 = 0.054 \text{ bar}$$

Mole fraction of benzene, $\chi_{\text{benzene}} = 1 - 0.60 = 0.40$

Vapour pressure of pure benzene, $P_{\text{benzene}}^{\circ} = 0.20 \text{ bar}$

partial vapour pressure of benzene,

$$P_{\text{benzene}} = 0.20 \times 0.40 = 0.08 \text{ bar}$$

Total vapour pressure of solution,

$$P_{\text{total}} = P_{\text{benzene}} + P_{\text{toluene}} = 0.08 + 0.054 = 0.134 \text{ bar}$$

b. Calculation of the composition of vapour phase

Mole fraction of benzene in vapour phase

$$\chi_{\text{benzene}}^{\text{v}} = \frac{P_{\text{benzene}}}{P_{\text{total}}} = \frac{0.08}{0.134} = 0.597$$

Mole fraction of toluene in vapour phase

$$\chi_{\text{toluene}}^{\text{v}} = \frac{0.054}{0.134} = 0.402$$

2. Let χ_A and χ_B are the mole fractions of liquids A and B in the solution, then

$$P_A = P_A^{\circ} \chi_A = 22 \chi_A$$

$$P_B = P_B^{\circ} \chi_B = P_B^{\circ} (1 - \chi_A) = 75 (1 - \chi_A)$$

$$P_A + P_B = 22 \chi_A + 75 (1 - \chi_A) = 48.5$$

$$\therefore \chi_A = 0.5; \chi_B = 1 - \chi_A = 1 - 0.5 = 0.5$$

Thus, the solution contains *equal moles of both liquids A and B*.

3. Mole fraction of liquid A, $\chi_l = \frac{0.2}{0.2 + 4.0} = 0.048$

Mole fraction of water, $\chi_w = 1.0 - 0.048 = 0.952$

$$0.210 = P_l^{\circ} \chi_l + P_w^{\circ} \chi_w$$

$$0.210 = P_l^{\circ} \times 0.048 + 0.198 \times 0.952$$

$$P_l^{\circ} = \frac{0.210 - 0.198 \times 0.952}{0.048} = 0.448 \text{ bar}$$

Exercise 2.2

1. Vapour pressure of ethyl alcohol (P_A°) = 59.2 torr

Vapour pressure of solution (P_{sol}) = 51.3 torr

Using Raoult's law

$$\frac{P_A^{\circ} - P_{\text{S}}}{P_A^{\circ}} = \chi_B \Rightarrow \frac{59.2 - 51.3}{59.2} = \chi_B \Rightarrow \chi_B = 0.133$$

$$\text{Molality } (m) = \frac{\chi_B}{1 - \chi_B} \times \frac{1000}{Mw_A}$$

[Mw_A = Molecular weight of ethyl alcohol = 46]

$$= \frac{0.133}{1 - 0.133} \times \frac{1000}{46}$$

$$\therefore m = 3.33$$

$$\left. \begin{array}{l} \text{Methyl alcohol}_{(B)} = 30 \times 0.8 \text{ g} = 24 \text{ g} \\ \text{Water}_{(A)} = 70 \times 1 \text{ g} = 70 \text{ g} \end{array} \right\}$$

$$\text{Total mass} = 94 \text{ g} \Rightarrow V_{\text{sol}} = \frac{94}{0.94} = 100 \text{ cm}^3$$

$$\chi_B = \frac{24/32}{24/32 + 70/18} = 0.16; \chi_A = 0.84$$

$$M = \frac{n_B}{V_L} = \frac{0.75}{100/1000} = 7.5$$

$$\Rightarrow m = \frac{\chi_B}{1 - \chi_B} \times \frac{1000}{Mw_A} = \frac{0.16}{0.84} \times \frac{1000}{18} = 10.58$$

$$3. \Delta T_f = \frac{K_f \times W_B \times 10000}{W_A \times Mw_B} = \frac{1.86 \times 30 \times 100}{70 \times 62} = 12.86$$

The solution will freeze at -12.86°C and therefore it will be suitable for car radiator.

$$4. \frac{P^{\circ} - P_{\text{S}}}{P_{\text{S}}} = \frac{n_2 \times Mw_1 \times 1000}{W_1 \times 1000}$$

$$\frac{17.39 - 17.0}{17.0} = \frac{\text{Molality} \times Mw_1}{1000}$$

$$\therefore \text{Molality} = \frac{0.39 \times 1000}{17 \times 18} = 1.275$$

For dilute solution, molarity = molality.

$$\therefore \pi = CRT = 1.275 \times 0.0821 \times 293 = 30.66 \text{ atm}$$

Also, for water vapours, $PV = nRT$

$$P = \frac{W_2}{V} \frac{RT}{Mw_2}$$

$$\frac{W_2}{V} = \frac{PMw_2}{RT} = \frac{17.0 \times 18}{760 \times 0.0821 \times 293}$$

$$\begin{aligned} \text{Density of H}_2\text{O(vapour)} &= 1.673 \times 10^{-2} \text{ g L}^{-1} \\ &= 1.673 \times 10^{-5} \text{ g mL}^{-1} \end{aligned}$$

Exercise 2.3

1. Find i (Van't Hoff factor) in two cases.

$$i = \frac{\Delta_f T}{K_f m} = \frac{5.5 - 3.1}{5.12 \times 1} = 0.469 \Rightarrow i < 1$$

So benzoic acid associates in benzene at low temperature since $i \approx 0.5 \Rightarrow$ it form a dimer.

$$i = \frac{\Delta_b T}{K_b m} = \frac{82.6 - 80.1}{2.53 \times 1} = 0.99 \approx 1 \Rightarrow i < 1$$

So benzoic acid neither associates nor it dissociates at high temperature.

Note: If $i > 1$, then solute dissociates.

2. (a, b, c, d)

Calculation of molecular weight of BOH:

Equivalent of the base = Equivalent of H_2SO_4 used

$$\frac{0.496}{M_{w_2}} \times 1 = 40 \times 10^3 \times \frac{1}{2} \times 2 \Rightarrow M_{w_2} = 1.24 \text{ g mol}^{-1}$$

$$\text{Now, } \Delta T_f = i \times K_f \times m$$

$$0.165 = i \times 1.86 \times \frac{1.5}{12.4} \times \frac{1000}{150}$$

$$i = \frac{0.165 \times 12.4}{1.86} = 1.1$$

$$i = \frac{\text{Total moles}}{\text{Initial moles}} = \frac{1 + \alpha}{1}$$

$$\therefore \alpha = 0.1$$

$$\text{So, } (\text{OH}) = C\alpha = 0.8 \times 0.1 = 8 \times 10^{-2}$$

$$\therefore p_{\text{OH}} = 1.1$$

$$\text{pH} = pK_w - p_{\text{OH}} = 14 - 1.1$$

$$\Rightarrow \text{pH} = 12.9$$

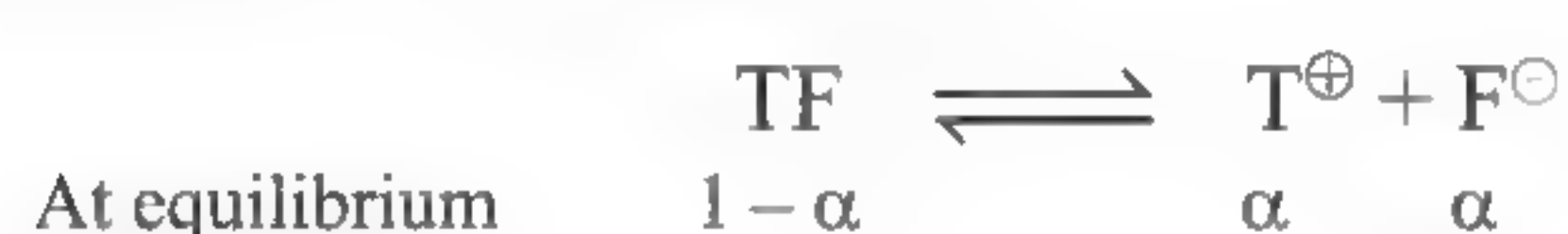
$$\text{So, } K_b = C\alpha^2 = 0.8 \times (0.1)^2 = 8 \times 10^{-3}$$

$$\text{Also, } \pi = iCRT$$

$$= 1.1 \times 0.8 \times 0.0821 \times 300$$

$$= 21.67 \text{ atm}$$

3. Ionization of TF gives

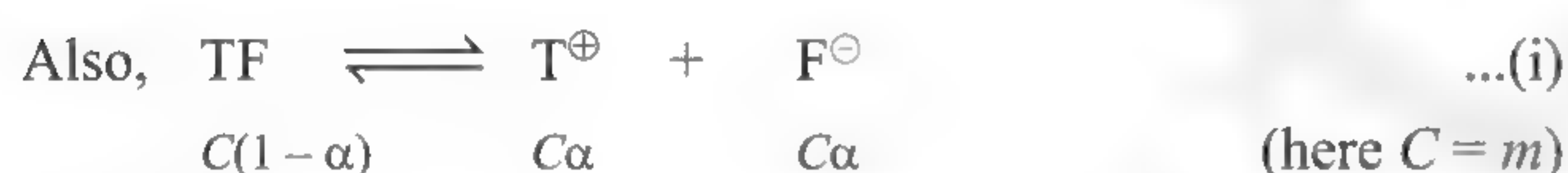


$$\text{Total moles} = 1 + \alpha$$

$$\therefore i = \frac{(\text{Total moles}) \text{ at equilibrium}}{\text{Initial moles}} = 1 + \alpha$$

$$\text{We know, } \Delta T_f = iK_f m \quad (\text{assume } m \approx \text{concentration in mol per litre})$$

$$\therefore m(1 + \alpha) = \frac{\Delta T_f}{K_f} = \frac{0.372}{1.86} = 0.2$$



$$\therefore [\text{T}^{\oplus}] = C\alpha = 10^{-1.5} = 0.0316 \text{ molar}$$

$$\text{Now, } m + m\alpha = 0.2 \text{ and } m\alpha = 0.0316$$

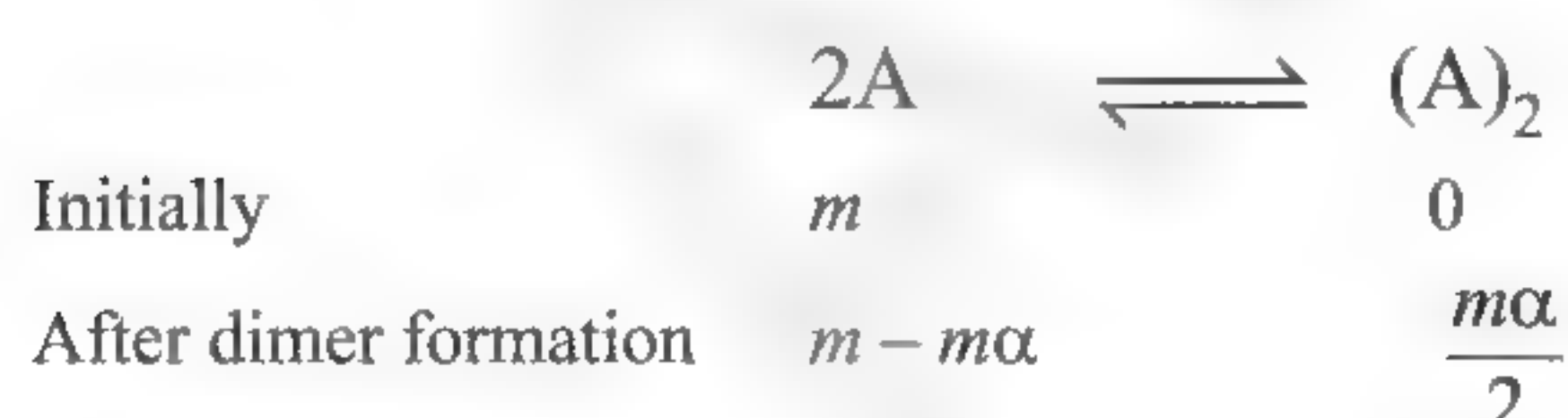
$$\Rightarrow m = 0.1684 \text{ and } m - m\alpha = 0.1684 - 0.0316 = 0.1368$$

Equilibrium constant K for reaction (i)

$$K = \frac{[\text{T}^{\oplus}][\text{F}^{\ominus}]}{[\text{TF}]} = \frac{[C\alpha][C\alpha]}{C(1 - \alpha)}$$

$$= \frac{(0.0316)^2}{0.1368} = 7.299 \times 10^{-3}$$

4. Let the degree of dimer formation be α . The reaction occurs as under



where m = molality = molarity (as also given)

Due to dimer formation, the resultant Molality will be

$$= (m - m\alpha) + \frac{m\alpha}{2}$$

$$\text{Van't Hoff factor, } i = \frac{(m - m\alpha) + \frac{m\alpha}{2}}{m}$$

$$i = \frac{m\left(1 - \frac{\alpha}{2}\right)}{m} \Rightarrow i = 1 - \frac{\alpha}{2}$$

As we known the elevation in boiling point

$$\Rightarrow \Delta T_b = K_b \times i \times C_m$$

$$= K_b \times \left(1 - \frac{\alpha}{2}\right) \times m, \text{ here } C_m = m$$

$$\Rightarrow \alpha = \frac{2(K_b m - \Delta T_b)}{K_b m}$$

The equilibrium constant for dimer formations

$$K_{\text{eq}} = \frac{[\text{A}_2]}{[\text{A}]^2} = \frac{\frac{m\alpha}{2}}{\{m(1 - \alpha)\}^2} = \frac{\frac{m\alpha}{2}}{m^2(1 - \alpha)^2}$$

$$= \frac{\alpha}{2m(1 - \alpha)^2} \quad \dots(i)$$

Putting the value of α in equation (i)

$$K_{\text{eq}} = \frac{2(K_b m - \Delta T_b)}{K_b m}$$

$$= \frac{2(K_b m - \Delta T_b)}{K_b m} = \frac{K_b(K_b m - \Delta T_b)}{(2\Delta T_b - K_b m)^2}$$

5. Mole fraction of A = χ

$$\therefore \text{Mole fraction of B} = 1 - \chi$$

According to Dalton rule:

$$\chi P_A^\circ + (1 - \chi)P_B^\circ = 85 \quad \dots(i)$$

Similarly when mole fraction of B = χ

$$(1 - \chi)P_A^\circ + \chi P_B^\circ = 95 \quad \dots(ii)$$

Adding equations (i) and (ii), we get

$$P_A^\circ + P_B^\circ = 180$$

$$1.25P_B^\circ + P_B^\circ = 180$$

$$\therefore P_B^\circ = 80 \text{ mm and } P_A^\circ = 100 \text{ mm}$$

Solving for χ , using equation (i)

$$\chi 100 + (1 - \chi)80 = 85$$

$$\text{or } \chi = \frac{1}{4}$$

$$\text{Hence } P_{\text{mix}} = P_A^\circ \chi_A + P_B^\circ \chi_B$$

$$P_{\text{mix}} = \frac{1}{4} \times 100 + \frac{3}{4} \times 80 = 25 + 60 = 85 \text{ mm}$$

Thus, the first trace of vapour will form at 85 mm. Compression of the first trace of vapour formed will be

$$\chi_A^{\text{v}} = \frac{P_A}{P_{\text{mix}}} = \frac{25}{85} = 0.294$$

$$\chi_B^{\text{v}} = \frac{P_B}{P_{\text{mix}}} = \frac{25}{85} = 0.706$$

$$6. Y_A = \frac{X_A P_A^\circ}{P_B^\circ + (P_A^\circ - P_B^\circ) X_A}$$

Subtracting X_A from both the sides, we get

$$Y_A - X_A = \frac{X_A P_A^\circ}{P_B^\circ + (P_A^\circ - P_B^\circ) X_A} - X_A$$

Now differentiating w.r.t, X_A we get

$$\frac{d(Y_A - X_A)}{dX_A} = \frac{P_A^\circ}{(P_A^\circ - P_B^\circ)X_A + P_B^\circ} - \frac{X_A P_A^\circ (P_A^\circ - P_B^\circ)}{\{P_B^\circ + (P_A^\circ - P_B^\circ)X_A\}^2} - 1$$

The value of X_A at which $Y_A - X_A$ has a minimum value can be obtained by putting the above derivative equal to zero. Thus, we have

$$\frac{P_A^\circ}{P_B^\circ + (P_A^\circ - P_B^\circ)X_A} - \frac{X_A P_A^\circ (P_A^\circ - P_B^\circ)}{\{P_B^\circ + (P_A^\circ - P_B^\circ)X_A\}^2} - 1 = 0$$

Solving for X_A , we get $X_A = \frac{\sqrt{P_A^\circ P_B^\circ} - P_B^\circ}{P_A^\circ - P_B^\circ}$ and hence

$$P = \sqrt{P_A^\circ P_B^\circ}$$

7. Loss in weight of solution $\propto P_s$

Loss in weight of solvent $\propto P^\circ - P_s$

$$\therefore \frac{P^\circ - P_s}{P_s} = \frac{\text{Loss in weight of solvent}}{\text{Loss in weight of solution}} \quad \dots(i)$$

$$\text{Also, } \frac{P^\circ - P_s}{P_s} = \frac{W_2 \times Mw_1}{Mw_2 \times W_1} \quad \dots(ii)$$

\therefore By equations (i) and (ii), we get

$$\frac{0.04}{2.5} = \frac{5 \times 18}{80 \times Mw_2} \Rightarrow Mw_2 = 70.31$$

8. Mole fraction of urea in its solution

$$= \frac{\frac{12}{60}}{\frac{12}{60} + \frac{140.4}{18}} \Rightarrow 0.025$$

Mole fraction of glucose

$$= \frac{\frac{18}{180}}{\frac{18}{180} + \frac{178.2}{18}} \Rightarrow 0.01$$

\therefore Mole fraction of glucose is less so vapour pressure above the glucose solution will be higher than the pressure above urea solution, so some H_2O molecules will transfer from glucose to urea side in order to make the solutions of equal mole fraction at equilibrium, let x moles H_2O transferred

$$\therefore \frac{0.2}{0.2 + 7.8 + x} = \frac{0.1}{0.1 + 9.9 - x} \Rightarrow x = 4$$

now mass of glucose solution

$$\Rightarrow 196.2 - 4 \times 18 \Rightarrow 124.2$$

$$\text{wt. \% of glucose} = \frac{18}{124.2} \times 100 \Rightarrow 14.49$$

$$9. \frac{P^\circ - P_s}{P_s} = \frac{n_2}{n_1} = \frac{w_2 \times Mw_1}{Mw_2 \times w_1}$$

$$\Rightarrow \frac{850 - 844.9}{844.9} = \frac{2 \times 76}{Mw_2 \times 100} \quad (Mw_1 (CS_2) = 76 \text{ g})$$

$$Mw_2 \approx 252; \quad n = \frac{252}{32} \approx 8 \quad (\text{Aw of S} = 32)$$

\therefore atomicity of sulphur is 8

$$10. \quad P = P_A^\circ x_A + P_B^\circ x_B \Rightarrow 100 \times \frac{1}{5} + 200 \times \frac{4}{5} \Rightarrow 189 \text{ torr}$$

$$y_A \text{ (composition of A in vapour phase)} = \frac{P_A^\circ x_A}{P}$$

$$\Rightarrow \frac{20}{180} \Rightarrow \frac{1}{9}, \therefore Y_B = \frac{8}{9}$$

For condensation $y_A = x_A^l$; $y_A = x_B^l$

$$P_{\text{Total}} = P_A^\circ x_A^l + P_B^\circ x_B^l$$

$$P_{\text{Total}} = 100 \times \frac{1}{9} + \frac{8}{9} \times 200 \Rightarrow 188.88 \text{ torr}$$

11. Let n_B mole of B present in 1 mole of mixture that has been vaporized. Thus, $y_B = \frac{n_B}{1}$

Mole fraction of B in the remaining liquid phase will be $x_B = \frac{1 - n_B}{1}$

$$x_B = \frac{P - P_T^\circ}{P_B^\circ - P_T^\circ} \quad \dots(1)$$

$$[\because P = P_T^\circ + (P_B^\circ - P_T^\circ)x_B]$$

$$\text{and } y_B = \frac{P_B}{P} \Rightarrow \frac{P_B^\circ x_B}{P} \quad \dots(2)$$

After substitution of values of x_B and y_B in (1) and (2)

$$\text{we get } 1 - n_B = \frac{P - P_T^\circ}{P_B^\circ - P_T^\circ} \quad \dots(3)$$

$$\text{and } n_B = \frac{(1 - n_B)P_B^\circ}{P} \quad \dots(4)$$

$$\text{or } n_B = \frac{P_B^\circ}{P + P_B}$$

$$\text{so } 1 - \frac{P_B^\circ}{P + P_B} = \frac{P - P_T^\circ}{P_B^\circ - P_T^\circ}$$

$$\Rightarrow P = \sqrt{P_B^\circ \cdot P_T^\circ} = \sqrt{100 \times 900}$$

$$\Rightarrow 300 \text{ torr}$$

12. For Na_3PO_4 , $i = 1 + 3\alpha = 1 + 3 \times 0.5$

$= 2.5$; for $MgSO_4$, $i = 1.6$

100 g solution contains 8.2 g Na_3PO_4 and 12 g $MgSO_4$

$$\Delta T_b = K_b \cdot m \cdot i =$$

$$K_b \cdot \left[\frac{\text{effective no. of moles of } (Na_3PO_4 + MgSO_4) \times 1000}{\text{mass of solvent (in g)}} \right]$$

$$\Delta T_b = 0.50 \left[\frac{\frac{8.2}{164} \times 2.5 + \frac{12}{120} \times 1.6}{79.8} \right] \times 1000$$

$$= 1.785^\circ\text{C}$$

$$T_b = 100 + 1.785 \Rightarrow 101.785^\circ\text{C}$$

$$13. \quad \Delta T_b = K_b \left(\frac{w_{\text{solute}}}{W_{\text{solvent}}} \times \frac{1}{M_{\text{solute}}} \right) \times 1000$$

$$1 = \frac{1000 \times 10}{100 \times M_{AB_2}} \Rightarrow M_{AB_2} = 100$$

similarly $M_{A_2B} = 140$

$$100 = M_A + 2 \cdot M_B$$

and $140 = 2 \cdot M_A + M_B$;

$$M_A = 60 \text{ and } M_B = 20$$

14. Given $\Delta H_{\text{fus.}} = 80 \text{ cal g}^{-1}$,

$$\Delta H_{\text{vap.}} = 540 \text{ cal g}^{-1}$$

We know, $\Delta T_b = K_b \times m$

and $\Delta T_f = K_f \times m$;

$$\text{Also } K = \frac{RT^2}{1000 \times \Delta H}$$

$$\therefore \frac{\Delta T_b}{\Delta T_f} = \frac{K_b}{K_f}$$

$$\Rightarrow \frac{RT_b^2}{1000 \times \Delta H_{\text{vap.}}} \times \frac{1000 \times \Delta H_{\text{fus.}}}{RT_f^2}$$

$$\Rightarrow \frac{\Delta T_b}{\Delta T_f} = \frac{T_b^2 \times \Delta H_{\text{fus.}}}{T_f^2 \times \Delta H_{\text{vap.}}}$$

$$\frac{0.1}{\Delta T_f} = \frac{373 \times 373 \times 80}{273 \times 273 \times 540}$$

$$\therefore \Delta T_f = 0.361$$

$$T_f = -0.361^\circ\text{C}$$

15. $\text{KI(aq)} + \text{AgNO}_3(\text{aq}) \rightarrow \text{AgI(s)} \downarrow + \text{KNO}_3(\text{aq})$



Initial : 0.3 mole 0.2 mole — —

Final “ 0.1 mole — 0.2 0.2

Total moles of solute ions = $(0.1 + 0.2) \times 2$ ($\because i = 2$)

$$[\text{Solute}] = \frac{0.6}{4}$$

$$\Delta T_f = K_f \cdot \frac{0.6}{4}$$

$$= 1.86 \times \frac{0.6}{4} = 0.279 \text{ K}$$

16. The given data are

$$P_{\text{water}} = 17.0 \text{ torr};$$

P_{total} (4 mole % solution)

$$= P_{\text{NH}_3} + P_{\text{water}} = 50.0 \text{ torr}$$

$$x_{\text{NH}_3} = 0.04 \text{ and } x_{\text{water}} = 0.96$$

Now according to Raoult's law;

$$P_{\text{water}} = x_{\text{water}} = P_{\text{water}}^\circ$$

$$= 0.96 \times 17.0 \text{ torr} = 16.32 \text{ torr}$$

Now Henry's law constant for ammonia is

$$K_H(\text{NH}_3) = \frac{P_{\text{NH}_3}}{x_{\text{NH}_3}} = \frac{33.68 \text{ torr}}{0.04} = 842 \text{ torr}$$

Hence, for 5 mole % solution, we have

$$P_{\text{NH}_3} = K_H(\text{NH}_3) x_{\text{NH}_3}$$

$$= (842 \text{ torr}) (0.05) = 42.1 \text{ torr}$$

$$P_{\text{water}} = P_{\text{water}}^\circ = x_{\text{water}}$$

$$= (17 \text{ torr}) (0.95) = 16.15 \text{ torr}$$

Thus, P_{total} (5 mole % solution)

$$P_{\text{NH}_3} + P_{\text{water}} = 42.1 + 16.15 = 58.25 \text{ torr}$$

17. $P = P_A^\circ x_A + P_B^\circ x_B$

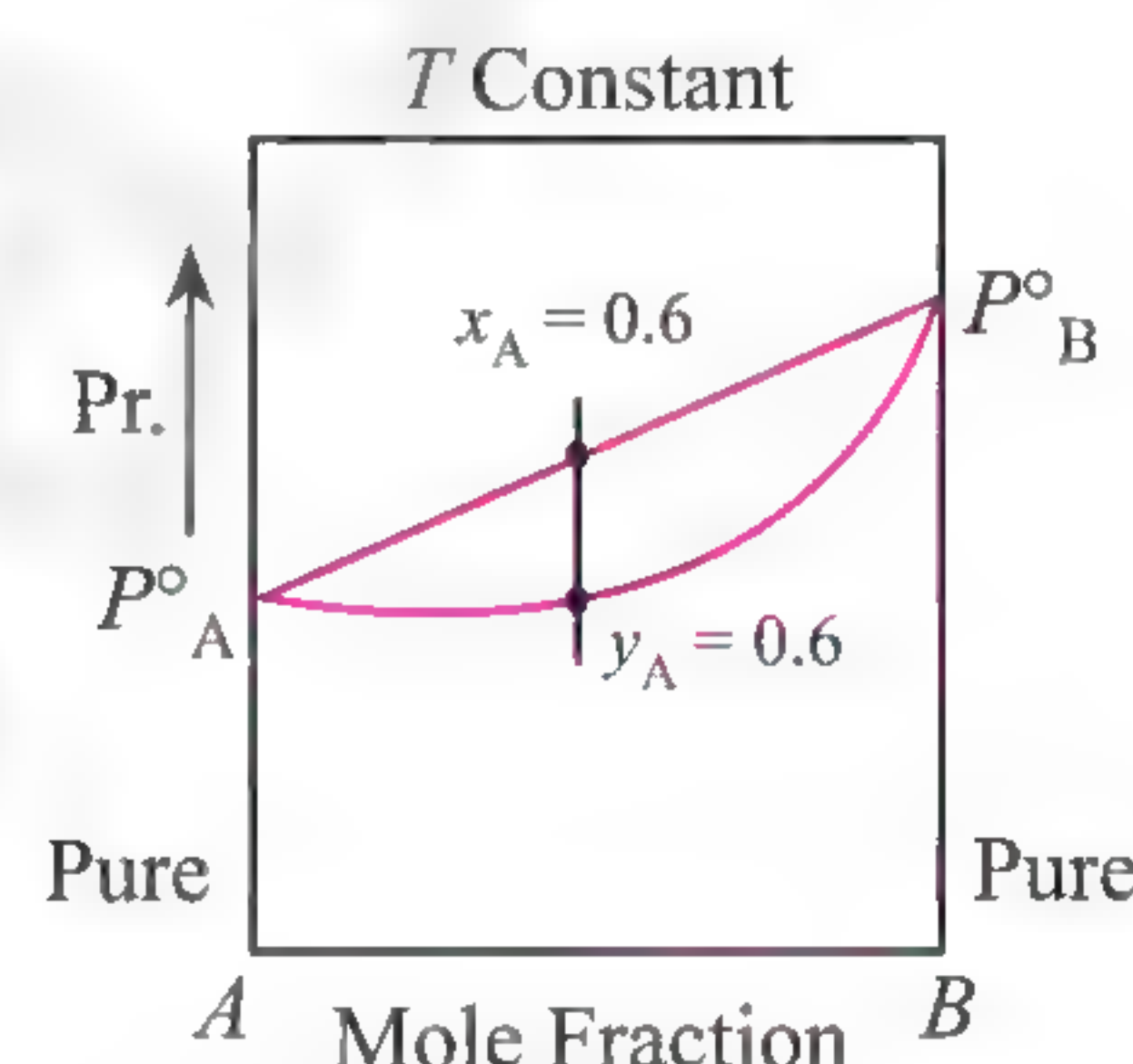
$$\Rightarrow 500 \times 0.6 + 800 \times 0.4$$

$$\Rightarrow 620 \text{ torr}$$

$$y_A = \frac{P_A}{P} \Rightarrow \frac{300}{620} = 0.48$$

$$y_B = 0.52$$

18. $P_A^\circ = 500$; $P_B^\circ = 800 \text{ torr}$



When most of the liquid has vaporized

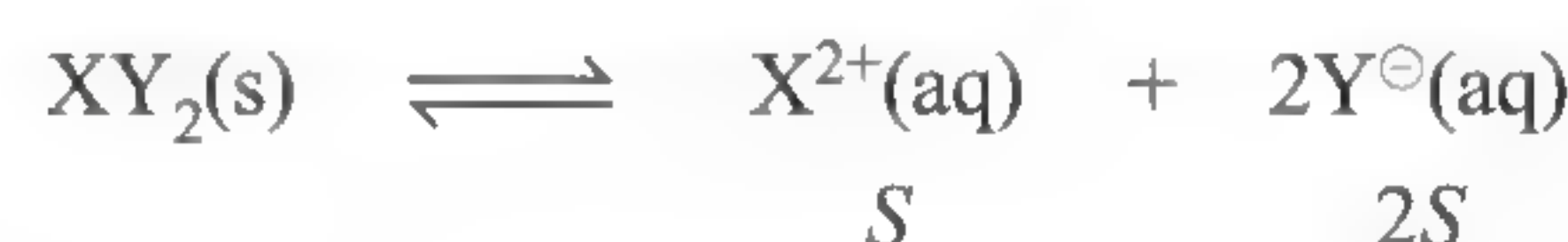
$$x_A = 0.6 \text{ (given), } y_A = 0.6$$

$$y_A = \frac{P_A^\circ x_A}{P_A^\circ x_A + P_B^\circ (1 - x_A)}$$

$$\Rightarrow 0.6 = \frac{500 \cdot x_A}{500x_A + 800(1 - x_A)}$$

$$x_A = 0.70; \quad x_B = 0.30$$

19. Let the solubility $\text{XY}_2(\text{s})$ at 30°C be $s \text{ mol L}^{-1}$.



$$\frac{P^\circ - P_s}{P_s} = \frac{n}{N} \quad (i = 3, \text{ if } 100\% \text{ ionization})$$

$$\frac{31.82 - 31.78}{31.78} = 3\chi_2, \chi_2 = 0.0004, \frac{n_2}{n_1} = 0.004$$

$$n_2 = 55.6 \times 0.004 = 0.0233$$

$$S = 0.0233 \text{ mol L}^{-1}$$

$$K_{\text{sp}}(\text{at } 30^\circ\text{C}) = (0.0233)(2 \times 0.0233)^2$$

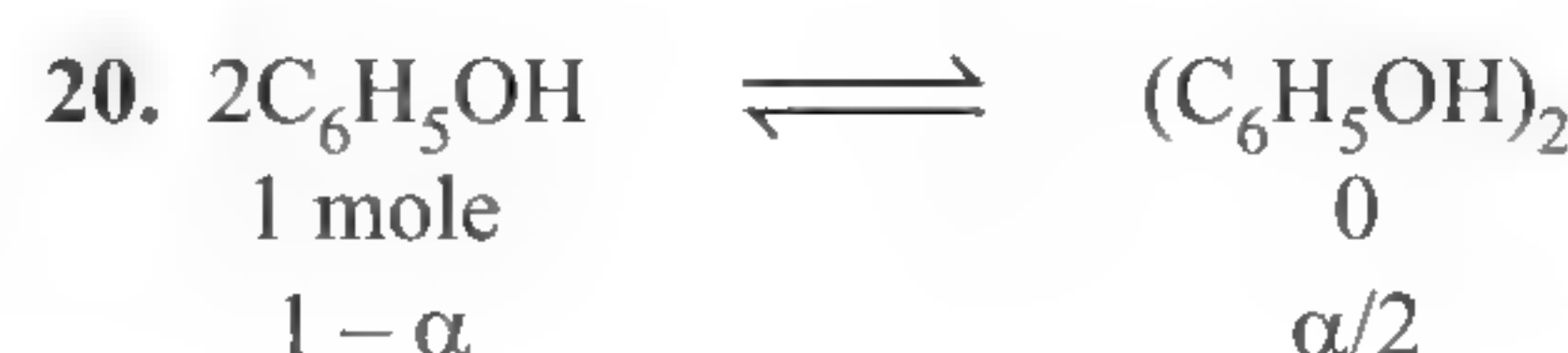
$$= 5.05 \times 10^{-5} (\text{mol L}^{-1})^3$$

$$K_{\text{sp}}(\text{at } 25^\circ\text{C}) = 3.56 \times 10^{-5} (\text{mol L}^{-1})^3$$

$$\text{Now, } \log \frac{K_{\text{sp}}(35^\circ\text{C})}{K_{\text{sp}}(25^\circ\text{C})} = \frac{\Delta H}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log \left(\frac{5.05 \times 10^{-5}}{3.56 \times 10^{-5}} \right) = \frac{\Delta H}{2.303 \times 8.314} \left(\frac{5}{303 \times 298} \right)$$

$$\Delta H = 52.5 \text{ kJ mol}^{-1}$$



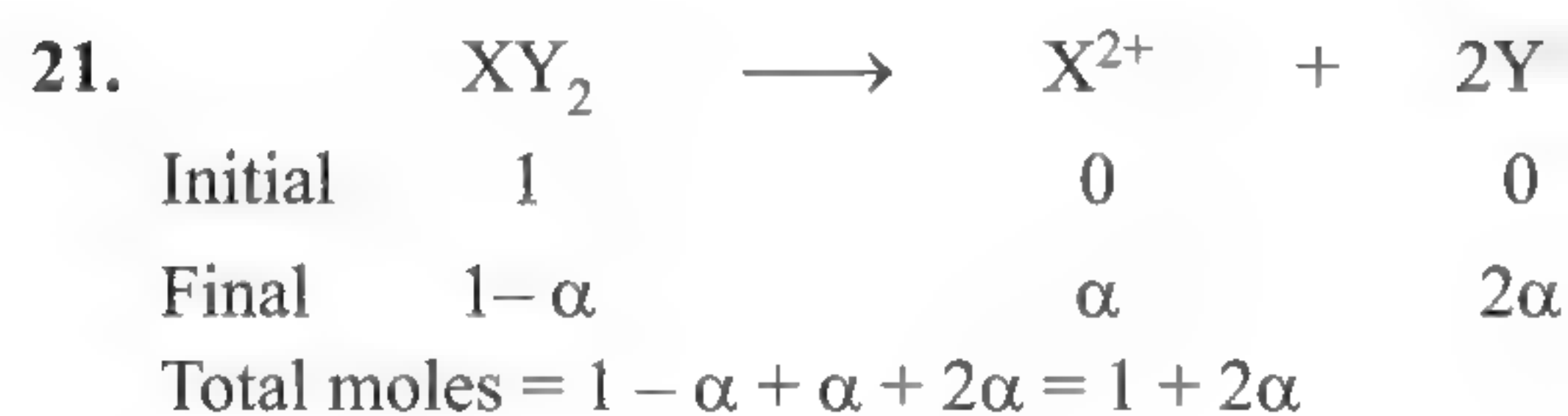
$$\text{Total} = 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}$$

$$i = \frac{1 - (\alpha/2)}{1} = 1 - \frac{\alpha}{2}$$

$$\Delta T_f = iK_f \frac{W_2 \times 1000}{Mw_2 \times W_1}$$

$$0.69 = \frac{i \times 5.12 \times 20 \times 10^3}{94 \times 1.0 \text{ kg}}$$

$$i = 1 - \frac{\alpha}{2}, \alpha = 0.733 = 73.3\%$$



$$i = \frac{1 + 2\alpha}{1} = 1 + 2 \times 0.5 = 2$$

$$n_{\text{H}_2\text{O}}(n_1) = \frac{1000}{18} = 55.55; n_{\text{urea}}(n_2) = \frac{3}{60} = 0.05$$

$$n_{\text{XY}_2}(n_3) = \frac{9}{Mw_3}$$

$$\chi_{\text{urea}} = \chi_2 = \frac{n_2}{n_1 + n_2 + n_3} = \frac{0.05}{55.55 + 0.05 + 9/Mw_3}$$

$$= \frac{0.05}{55.6 + 9/Mw_3}$$

$$\chi_{\text{XY}_2} = \chi_3 = \frac{9/Mw_3}{55.6 + 9/Mw_3}$$

$$\frac{P^\circ - P_s}{P^\circ} = \chi_2 + i \chi_3$$

$$\frac{330 - 328.515}{330} = \frac{0.05}{55.6 + 9/Mw_3} + 2 \times \frac{9/Mw_3}{55.6 + 9/Mw_3}$$

$$0.0045 = \frac{1}{55.6 + 9/Mw_3} \left(0.05 + \frac{2 \times 9}{Mw_3} \right)$$

$$\text{Solve, } Mw_3 = 89.6$$

$$\text{VD} = \frac{89.6}{2} = 44.8$$

Exercises

Single Correct Answer Type

1. (2) Hydrogen will have higher value of K_H because if gas has higher solubility, its K_H value is lower.
2. (2) Henry's law is only applicable when the temperature is low.
3. (2) At 1 bar pressure,

$$\text{Partial pressure of } \text{O}_2 (p_{\text{O}_2}) = \frac{1}{5} \times 1 \text{ bar} = 0.2 \text{ bar}$$

$$\text{Partial pressure of } \text{N}_2 (p_{\text{N}_2}) = \frac{4}{5} \times 1 \text{ bar} = 0.8 \text{ bar}$$

Applying Henry's law.

$$p_{\text{O}_2} = K_H(\text{O}_2) \times x_{\text{O}_2} \quad \text{or} \quad x_{\text{O}_2} = \frac{p_{\text{O}_2}}{K_H(\text{O}_2)}$$

$$p_{\text{N}_2} = K_H(\text{N}_2) \times x_{\text{N}_2} \quad \text{or} \quad x_{\text{N}_2} = \frac{p_{\text{N}_2}}{K_H(\text{N}_2)}$$

$$\therefore \frac{x_{\text{O}_2}}{x_{\text{N}_2}} = \frac{p_{\text{O}_2}}{K_H(\text{O}_2)} \times \frac{K_H(\text{N}_2)}{p_{\text{N}_2}} = \frac{p_{\text{O}_2}}{p_{\text{N}_2}} \times \frac{K_H(\text{N}_2)}{K_H(\text{O}_2)}$$

$$= \frac{0.2 \text{ bar}}{0.8 \text{ bar}} \times \frac{6.60 \times 10^7 \text{ torr}}{3.30 \times 10^7 \text{ torr}} = \frac{1}{2}$$

$$\text{i.e., } x_{\text{N}_2} : x_{\text{O}_2} = 2 : 1$$

4. (2)

Gas	Temperature	K_H (K bar)
He	293	144.97
N ₂	293	76.48
O ₂	293	34.86

Higher the value of Henry's Law constant, the lower is the solubility of the gas in the liquid.

5. (2) $m = kP$

$$\ln m = \log P + \log K$$

$$\log m = \log P + \log K$$

Comparing with $y = mx + c$ we get graph in option (2).

6. (1) According to Henry's law partial pressure of gas in the solution is proportional to the mole fraction of gas in the solution.

$$p = K_H x$$

Hence, (1) mole fraction is the correct choice.

7. (2) 30 g As is present in 10^6 g of water

$$\therefore \text{Percentage of mass of As} = \frac{30 \times 100}{10^6} = 3.0 \times 10^{-3}$$

$$m = \frac{W_2 \times 1000}{Aw_2 \times W_1} = \frac{30 \times 1000}{75 \times 10^6} = 0.4 \times 10^{-3} = 4.0 \times 10^{-2}$$

8. (1) According to Henry's law

$$\text{concentration} = K_H \times p$$

$$= 3.0 \times 10^{-2} \times 5 \text{ mol L}^{-1} = 0.15 \text{ M}$$

9. (1) Mole fraction of liquid A, $\chi_l = \frac{0.2}{0.2 + 4.0} = 0.048$

$$\text{Mole fraction of water, } \chi_w = 1.0 - 0.048 = 0.952$$

$$0.210 = P_l^\circ \chi_l + P_w^\circ \chi_w$$

$$0.210 = P_l^\circ \times 0.048 + 0.198 \times 0.952$$

$$P_l^\circ = \frac{0.210 - 0.198 \times 0.952}{0.048} = 0.448 \text{ bar}$$

$$10. (1) \chi_A^v = 0.36 = \frac{P_A^\circ \chi_A}{P_A^\circ \chi_A + P_B^\circ (1 - \chi_A)}$$

$$\Rightarrow 0.36 \times P_B^\circ (1 - \chi_A) = 0.64 P_A^\circ \chi_A$$

$$\Rightarrow \chi_A = 0.43$$

$$11. (2) P_{\text{total}} = P_A^\circ \chi_A + P_B^\circ \chi_A$$

$$\Rightarrow 500 = P_A^\circ \times \frac{1}{2} + P_B^\circ \times \frac{1}{2} \Rightarrow P_A^\circ + P_B^\circ = 1000 \quad \dots(i)$$

$$550 = P_A^\circ \times \frac{1}{4} + P_B^\circ \times \frac{3}{4} \Rightarrow P_A^\circ + 3P_B^\circ = 2200$$

...(ii)

Solving Eqs. (i) and (ii), we get

$$\Rightarrow P_A^\circ = 400 \text{ mm Hg and } P_B^\circ = 600 \text{ mm Hg}$$

12. (3) $P_{\text{total}} = 254 - 119\chi_A$
 For P_A° : put $\chi_A = 1 \Rightarrow P_A^\circ = 135 \text{ mm Hg}$
 For P_B° : put $\chi_A = 0 \Rightarrow P_B^\circ = 254 \text{ mm Hg}$
13. (1) Follows from the definition of solutions showing negative deviations.
14. (1) $\chi_A^V = \frac{P_A^\circ \chi_A}{P_{\text{total}}} = \chi_1 = \frac{P_A^\circ \chi_2}{P_{\text{total}}} \text{ or } P_{\text{total}} = P_A^\circ \frac{\chi_2}{\chi_1}$
15. (1) $\left. \begin{array}{l} P_{\text{CH}_3\text{OH}} = 92 \text{ torr} \\ P_{\text{sol}} = 23 \text{ torr} \end{array} \right\} = \chi_B = \frac{92 - 23}{92} = 0.75; \chi_A = 0.25$
 $\chi_A = 0.25$
16. (2) $\left. \begin{array}{l} P_{\text{benzene}}^\circ = 268 \text{ torr} \\ P_{\text{sol}} = 167 \text{ torr} \end{array} \right\} \chi_B = \frac{268 - 167}{268} = 0.377$
 $\chi_B = \frac{n_B}{n_A + n_B} \Rightarrow \frac{n_B}{n_A} = 0.605$
17. (2) $\left. \begin{array}{l} P_A^\circ = 0.8 \text{ atm} \\ P_{\text{sol}} = 0.6 \text{ atm} \end{array} \right\} \chi_B = \frac{0.8 - 0.6}{0.8} = 0.25$
18. (1) $P_A = 40 \text{ mm Hg}; P_A = P_A^\circ \chi_A = 32 \Rightarrow \chi_A = 0.8; \chi_B = 0.2$
19. (2) Positive deviations from Raoult's law are noticed when
 i. Experimental value of vapour pressure of mixture is more than calculated value.
 ii. Experimental value of boiling point of mixture is less than the calculated value.
 iii. $\Delta_{\text{mixing}} H = +ve$
 iv. $\Delta_{\text{mixing}} V = +ve$
20. (2) A characteristic of azeotropic mixture.
21. (1) The definition of azeotropic mixture.
22. (1) The interparticle forces in between CHCl_3 and acetone increase due to H-bonding and thus $\Delta_{\text{mixing}} V$ becomes negative.
23. (4) All get dissolved with the evolution of heat.
24. (3) No changes in interparticle forces as both are non-polar.
25. (1) $P_S = P^\circ \chi_2$
26. (4) $\text{C}_2\text{H}_5\text{OH}$ show H-bonding as well as polarity both.
27. (3) Vapour pressure of methanol + Water mixture $>$ VP of H_2O but less than that of methanol.
28. (3) For an ideal solution
 $\Delta_{\text{mixing}} H = 0; \Delta_{\text{mixing}} V = 0$ and it should obey Raoult's law.
29. (1) Mixing of benzene and toluene does not involve any kind of decrease or increase in interaction forces in between molecules.
30. (2) The temperature at which a liquid boils increases with increase in pressure.
31. (2) $\frac{P^\circ - P_S}{P^\circ} = \text{Mole fraction of solute} = \chi_2$
32. (1) $P^\circ - P_S \propto \text{loss in weight of water chamber}$
 and $P_S \propto \text{loss in weight of solution chamber}$

$$\frac{P^\circ - P_S}{P_S} = \frac{n_2}{n_1} = \frac{W_2 \times Mw_1}{Mw_2 \times W_1}$$

 or $\frac{0.04}{2.50} = \frac{5 \times 18}{Mw_2 \times 180}$
 $\therefore Mw_2 = 31.25$

$$33. (2) P_m = 160 \times \frac{1}{2} + 60 \times \frac{1}{2} = 110 \text{ mm}$$

34. (4) Azeotropic mixture of HCl contains 20.4% HCl.

$$35. (2) P_{\text{EtOH}} = P_{\text{EtOH}}^\circ \times \text{Mole fraction of EtOH in liquid phase} \\ = P_T \times \text{Mole fraction of EtOH in vapour phase}$$

Thus, mole fraction of EtOH in vapour phase

$$= \frac{P'}{P_T} = \frac{4.556}{4.556 + 2.619} = 0.635$$

$$36. (2) \therefore P^\circ - P_s = P^\circ \times \text{Mole fraction of solute} \\ 10 = P^\circ \times 0.2$$

$$20 = P^\circ \times \chi_2$$

$$\therefore \chi_2 = 0.4 \Rightarrow \chi_1 (\text{solvent}) = 1 - 0.4 = 0.6$$

$$37. (4) \chi'_T (\text{vap}) = \frac{\chi_T P_T^\circ}{\chi_T P_T^\circ + \chi_B P_B^\circ} = 0.4$$

$$38. (2) P_{\text{total}} = P_A^\circ \chi_A + P_B^\circ \chi_B \\ = 210 \text{ mm} > 200 \text{ mm}$$

Vapour pressure is decreased.

$$39. (1) p = P_B^\circ \chi_B \text{ (B = Benzene acts as solvent)}$$

$$\chi_B = \frac{p}{P_B^\circ} = \frac{167}{268} = 0.623$$

$$\chi_{\text{solute}} = 1 - \chi_B = 0.377$$

40. (1)

$$41. (1) \chi_1 = \frac{P_A^\circ \chi_A}{P_{\text{Total}}} = \frac{P_A^\circ \chi_2}{P_{\text{Total}}}$$

$$\therefore P_{\text{Total}} = \frac{P_A^\circ \chi_2}{\chi_1}$$

$$42. (1) \frac{\Delta P}{P^\circ} = 0.50 = \frac{n_1 i}{n_1 i + n_2}$$

$$0.50 = \frac{2i}{2i + 3}$$

$$i = 1.5 = 1 + x$$

$$x = 0.5$$

Hence, 2 mol NaCl will exist as 1 mol Cl^\ominus due to 50% ionization.

$$43. (3) P_{\text{Total}} = P_A^\circ \chi_A + P_B^\circ \chi_B \\ = P_A^\circ \chi_A + P_B^\circ (1 - \chi_A) \\ = P_B^\circ - (P_B^\circ - P_A^\circ) \chi_A$$

$$\text{Given equation} = 254 - 119\chi_A$$

Compare with the given equation,

$$\therefore P_B^\circ = 254, P_B^\circ - P_A^\circ = 119$$

$$\therefore P_A^\circ = 254 - 119 = 135$$

44. (4) (i) Plot AD shows vapour pressure of B containing A volatile component.

(ii) Plot BC shows vapour pressure of A containing B volatile component.

(iii) Plot CD shows vapour pressure of liquid solution containing A and B.

(iv) Volatile components, $P = P_A + P_B$, $EH = EF + EG$.

$$45. (1) P_{\text{Total}} \times x_A = P_A \\ \frac{1}{P_{\text{Total}}} = x_A \times \frac{1}{P_A}$$

When $\frac{1}{P_{\text{Total}}}$ is plotted against x_A , we get straight

line passing through origin having slope of $\frac{1}{P_A}$

46. (1) A characteristic of azeotropes.

47. (3) $P_M = P_{C_5H_{12}}^\circ \cdot X_{C_5H_{12}}^\circ + P_{C_6H_{14}}^\circ \cdot X_{C_6H_{14}}^\circ$

Thus, $P_M = 440 \times \frac{1}{4} + 120 \times \frac{4}{5} = 184$

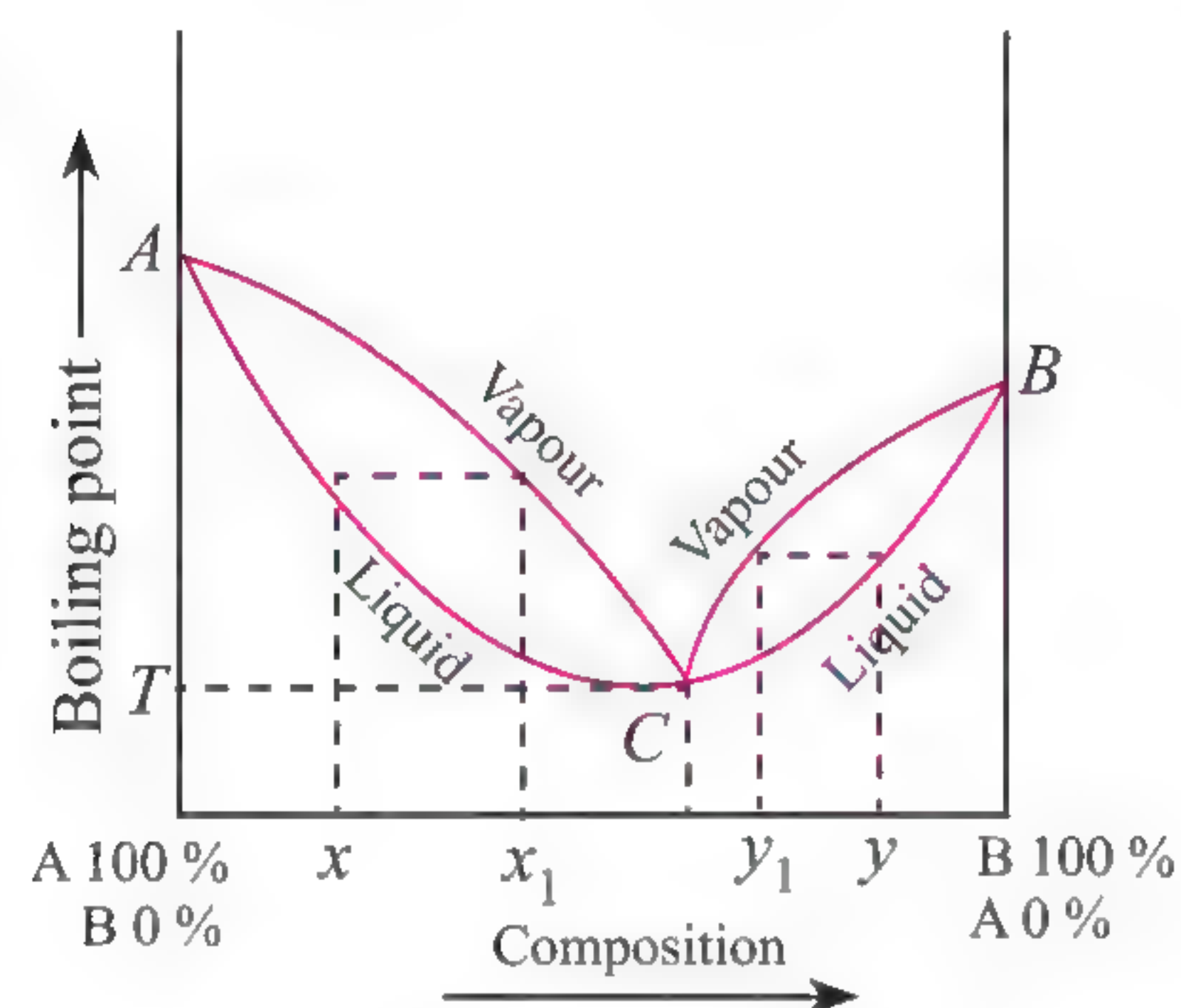
Now, $P_{C_5H_{12}} = P_{C_5H_{12}}^\circ \cdot X_{C_5H_{12}(l)} = P_M \cdot X_{C_5H_{12}(g)}$

$\therefore 440 \times \frac{1}{5} = 184 \times X_{C_5H_{12}(g)}$

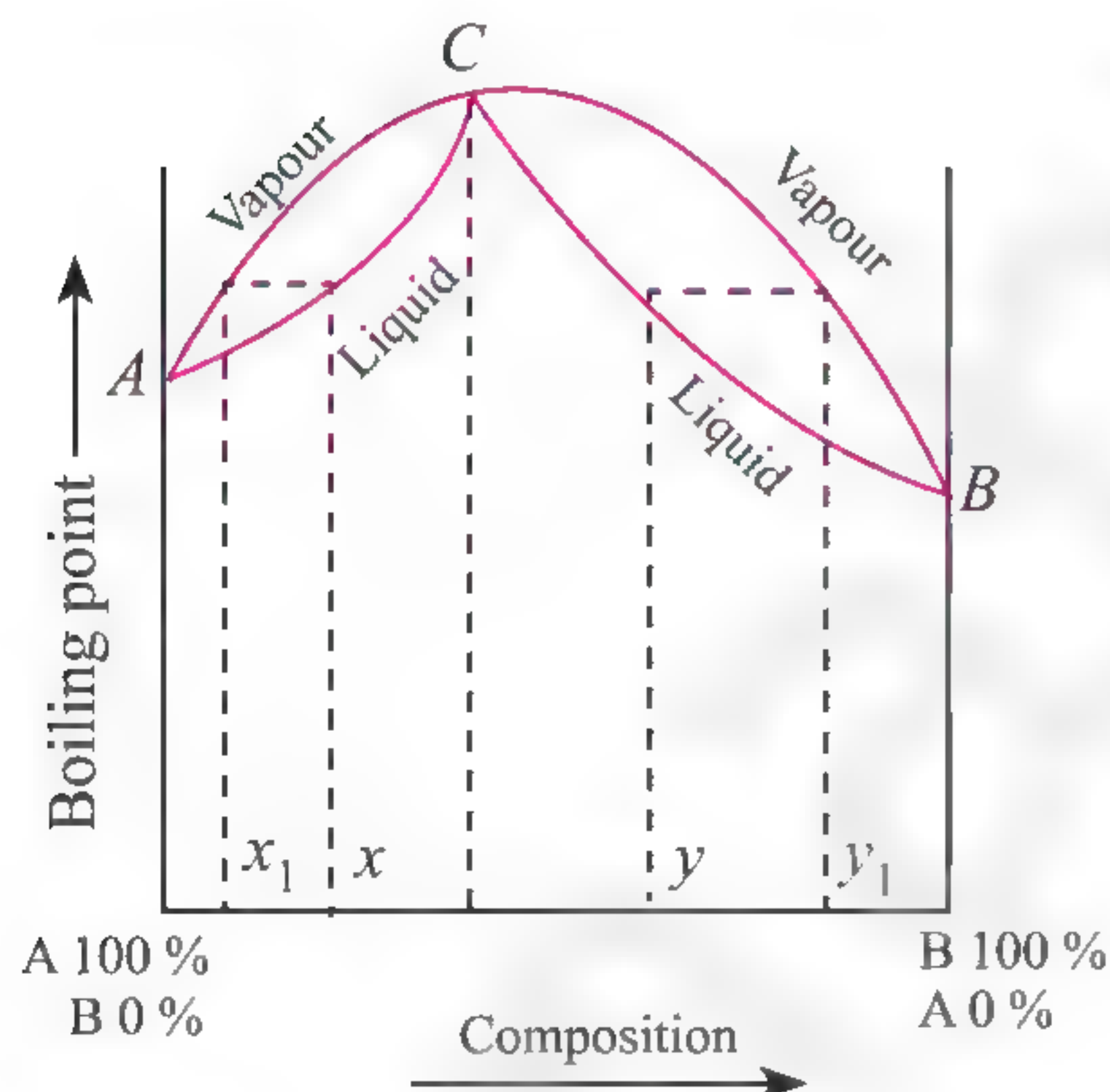
$\therefore X_{C_5H_{12}(g)} = 0.478.$

48. (2) Substances of high vapour pressure (e.g., gasoline) evaporates more quickly than substances of low vapour pressure (e.g., motor oil).

49. (2)



Non-ideal solution with positive deviation



Non-ideal solution with negative deviation

50. (3) $P_A^\circ X_A = P_T \cdot Y_A$

$\therefore \frac{X_A}{Y_A} = \frac{P_T}{P_A^\circ} < 1$ ($\because P_T < P_A^\circ$)

$X_A < Y_A.$

51. (2) Given $P_1 = 19 \text{ mm Hg}$, $P_2 = 760 \text{ mm Hg}$;

$\Delta H_{\text{vap.}} = 40670 \text{ J/mol}$

Applying Clausius-Clapeyron's equation

$\log \frac{P_1}{P_2} = \frac{\Delta H_{\text{vap}}}{2.303 \times R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$

or $\log \frac{760}{19} = \frac{40670}{2.303 \times 8.3} \left(\frac{373 - T_1}{T_1 \times 373} \right)$

on solving, we get $T_1 = 291.4 \text{ K}$

52. (1) $x_A = \frac{1}{1+3} \Rightarrow \frac{1}{4}; \quad x_B = \frac{3}{4};$

$\frac{y_A}{y_B} = \frac{P_A^\circ}{P_B^\circ} \times \frac{x_A}{x_B}$

$\frac{y_A}{(1-y_A)} = \frac{1}{3} \times \frac{1}{3} = \frac{1}{9}$

$y_A = \frac{1}{10} = 0.1$

53. (4) $\because (T_b)_{\text{Solvent}} < (T_b)_{\text{Solution}};$

$\therefore \Delta S_{\text{Solvent}} > \Delta S_{\text{Solution}}$

$(\Delta H_{\text{Solution}}) = \Delta H_{\text{Solvent}}$

[Only solvent participate in vaporisation]

[Due to elevation in BP of solution]

54. (4) $(\Delta_f H_{\text{vap}})_{\text{Solvent}} \approx (\Delta_f H_{\text{vap}})_{\text{Solvent}}$

[Because similar intermolecular forces are involved in both cases].

$\therefore (T_b)_{\text{Solvent}} > (T_b)_{\text{Solution}}$

$(\Delta S_{\text{vap}})_{\text{Solution}} < (\Delta S_{\text{vap}})_{\text{Solvent}}$

55. (3) $T_B^\circ > T_A^\circ$ [From diagram] $B \rightarrow \text{Residue}$

$A \rightarrow \text{Distillate}$

56. (4) On changing external pressure, composition of azeotrope alters.

57. (2) After mixing HNO_3 and H_2O , intermolecular force of attraction increase.

58. (4) $\because P_{\text{Ideal solution}} = \frac{1}{4} \times 100 + 80 \times \frac{3}{4} = 85 \text{ mm Hg}$

$< P_{\text{Solution}} (90 \text{ mm Hg})$

\therefore Solution show positive deviation from Raoult's law.

59. (2) $P_A = P_A^\circ X_A, \quad (P_A^\circ \text{ and } P_B^\circ = \text{V.P. of pure } A \text{ and } B)$

$P_B = P_B^\circ X_B$

$Y_A = \frac{P_A}{P_A + P_B}$

$\Rightarrow \frac{P_A^\circ X_A}{P_A^\circ X_A + P_B^\circ (1 - X_A)}$

$\Rightarrow Y_A = \frac{P_A^\circ X_A}{X_A (P_A^\circ - P_B^\circ) + P_B^\circ}$

$\Rightarrow \frac{1}{Y_A} = \left(\frac{P_A^\circ - P_B^\circ}{P_A^\circ} \right) + \frac{P_B^\circ}{P_A^\circ} \cdot \frac{1}{X_A}$

So, slope is $\frac{P_B^\circ}{P_A^\circ}$ and intercept $= \frac{P_A^\circ - P_B^\circ}{P_A^\circ}$

60. (3) For an ideal solution $\Delta H_{\text{mix}} = 0$ and ΔS_{mix} is always positive so ΔG_{mix} is negative.

$$61. (4) \text{ Molality of solution} = \frac{P^\circ - P}{P} \times \frac{1000}{M}$$

$$\Rightarrow \frac{40.18 - 40}{40} \times \frac{1000}{18} \Rightarrow 0.25$$

1000 g water present with 45 g glucose or 100 g solution has 4.31 g glucose and 95.69 g H₂O. Final molality is 0.5, 1000 g solvent contain 90 g glucose or 4.31 g glucose present with $\frac{1000}{90} \times 4.31 = 47.88$ g

H₂O Mass of ice formed = 95.69 – 47.88 = 47.8 g

$$62. (4) \Delta T_f = 2.55^\circ\text{C} = K_f \cdot m \therefore m = \frac{2.55}{K_f}$$

$$\Delta T_b = K_b \cdot m \Rightarrow \Delta T_b$$

$$= 2.55 \times \frac{K_b}{K_f} = 2.55 \times \frac{0.52}{1.86}^\circ\text{C} = 0.7^\circ\text{C}$$

$$\Rightarrow T_b = 100 + 0.7 = 100.7^\circ\text{C}$$

$$63. (3) \chi_B = \frac{\Delta P}{P_A^\circ} = 0.018$$

$$\Delta T_b = K_b \cdot m \Rightarrow 0.54 \times 1, K_b = 0.54$$

$$m = \frac{\chi_B}{1 - \chi_B} \times \frac{1000}{Mw_A}$$

$$m = \frac{0.018}{0.982} \times \frac{1000}{18} = 1.0 \Rightarrow \Delta T_b = K_b \times m = 0.54^\circ\text{C}$$

$$64. (3) \pi = C_{\text{effective}} RT;$$

Check yourself that

$$\begin{array}{ccc} n_{\text{sucrose}} & < & n_{\text{glucose}} < n_{\text{urea}} \\ (Mw = 342) & & (Mw = 180) & (Mw = 60) \end{array}$$

$$(\pi_3 < \pi_1 < \pi_2) \text{ or } (\pi_2 > \pi_1 > \pi_3)$$

$$65. (2) \pi = CRT$$

$$\Rightarrow 1.23 = \frac{0.6/Mw_B}{0.1} \times 0.0821 \times 300$$

$$\Rightarrow Mw_B = 120.15 \text{ g mol}^{-1}$$

$$66. (3) \text{ Isotonic solutions: Same osmotic pressure (i.e., same } C_{\text{effective}} \text{ and assume } c \approx m)$$

$$\Rightarrow \frac{5/342}{95/1000} = \frac{1/Mw_2}{99/1000} \Rightarrow Mw_2 = 65.64 \text{ g mol}^{-1}$$

$$67. (4) \frac{\Delta P}{P_A^\circ} = \chi_B = 0.05 \text{ (given)}$$

$$0.05 = \frac{n_B}{n_B + n_A} = \frac{n_B}{n_B + \frac{171}{18}}$$

$$\Rightarrow n_B = 0.5 \Rightarrow W_{\text{urea}} = 0.5 \times 60 = 30 \text{ g}$$

(Mw urea = 60 g)

$$68. (4) \frac{P_A^\circ - 60}{P_A^\circ} = \chi_B = 0.2 \Rightarrow P_A^\circ = 75 \text{ mm Hg}$$

$$69. (3) \frac{\Delta P}{P^\circ} = \chi_B \Rightarrow \frac{\Delta P}{P^\circ} = \chi_B = \frac{5/Mw_B}{5/Mw_B + 100/18}$$

$$\Rightarrow Mw_B = 179.28 \text{ g mol}^{-1}$$

$$70. (3) \Delta T_b = K_b \cdot m = 0.513 \times \frac{0.1}{200/1000} = 0.256^\circ\text{C}$$

$$\Rightarrow T_b = 100 + 0.256 = 100.256^\circ\text{C}$$

$$71. (2) \Delta T_b = iK_b m = 2 \times 0.52 \times 1 = 1.04^\circ\text{C}$$

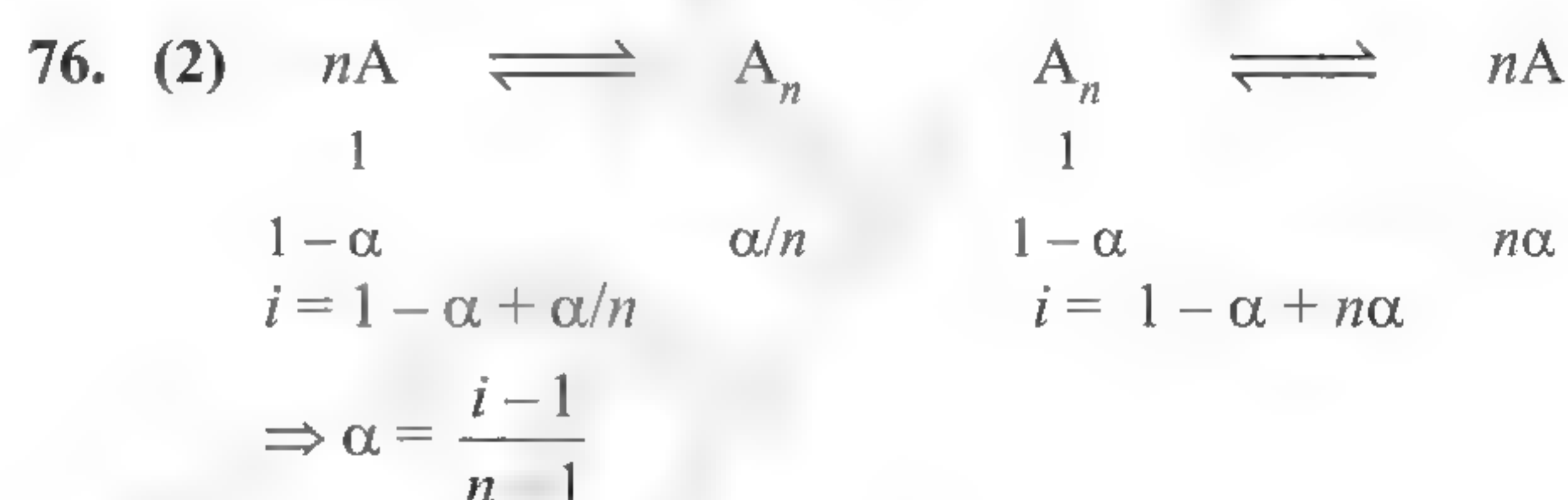
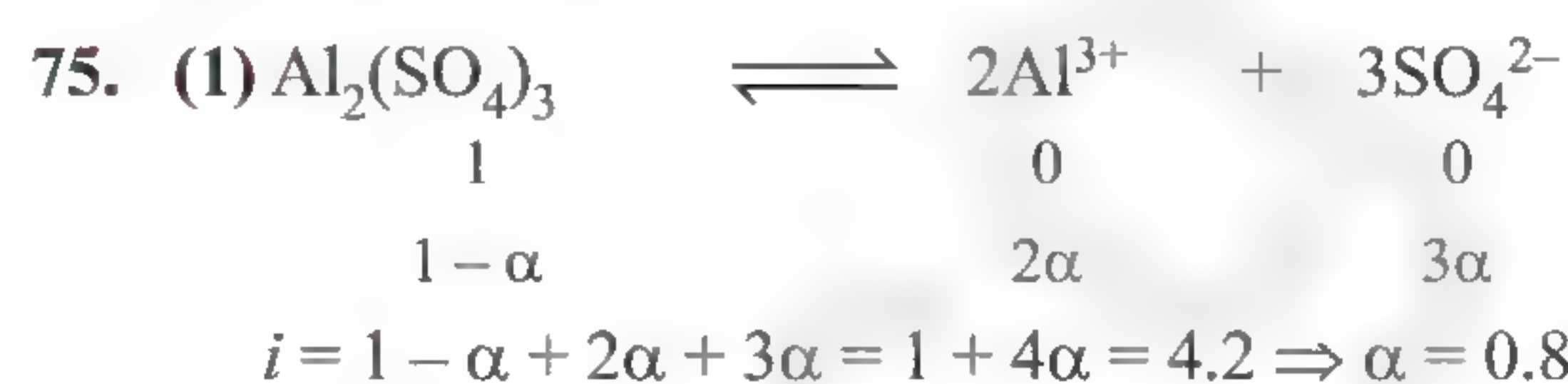
$$\Rightarrow T_b = 100 + \Delta T_b = 101.04^\circ\text{C}$$

$$72. (3) \Delta T_f \text{ depends on } m_{\text{eff}} \text{ and } \Delta T_f = iK_f m$$

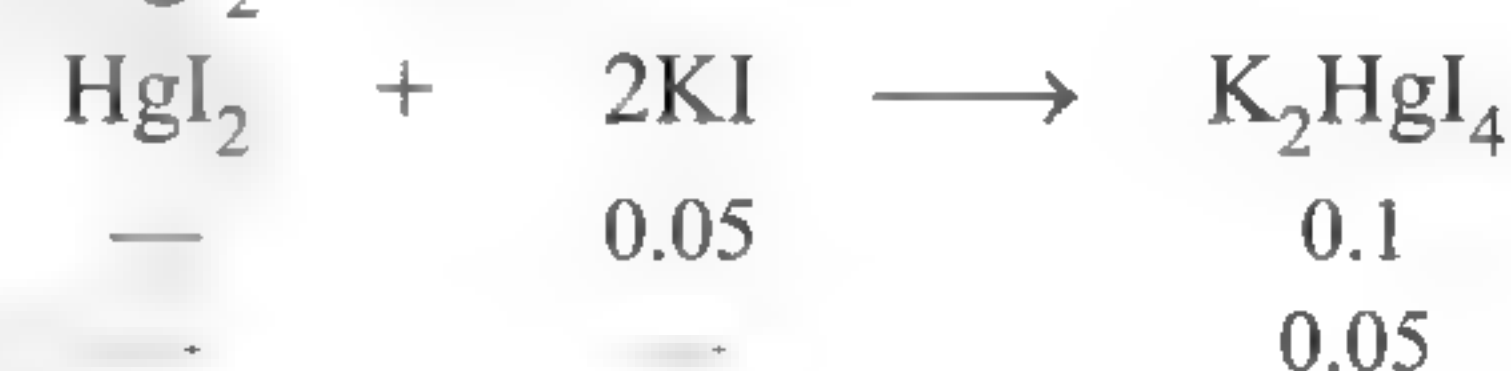
$$\text{Urea: } i = 1; \text{ NaCl: } i = 2; \text{ Na}_2\text{SO}_4: i = 3$$

$$73. (3) i = \frac{60}{100} = 1 - \frac{\alpha}{2} \Rightarrow \alpha = 80\%$$

$$74. (2) \Delta T_f = iK_f m \Rightarrow 0.704 = i \times 1.86 \times 0.19 \Rightarrow i = 2$$



$$77. (2) \text{ When HgI}_2 \text{ is added to KI:}$$



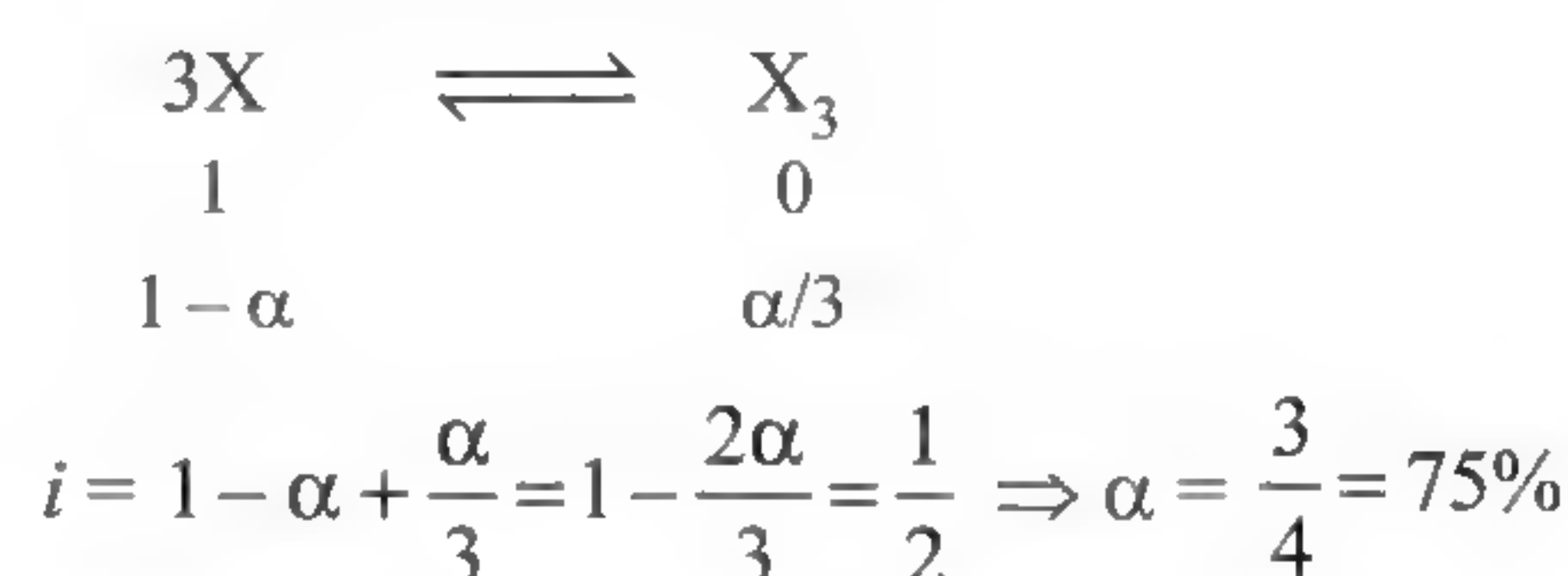
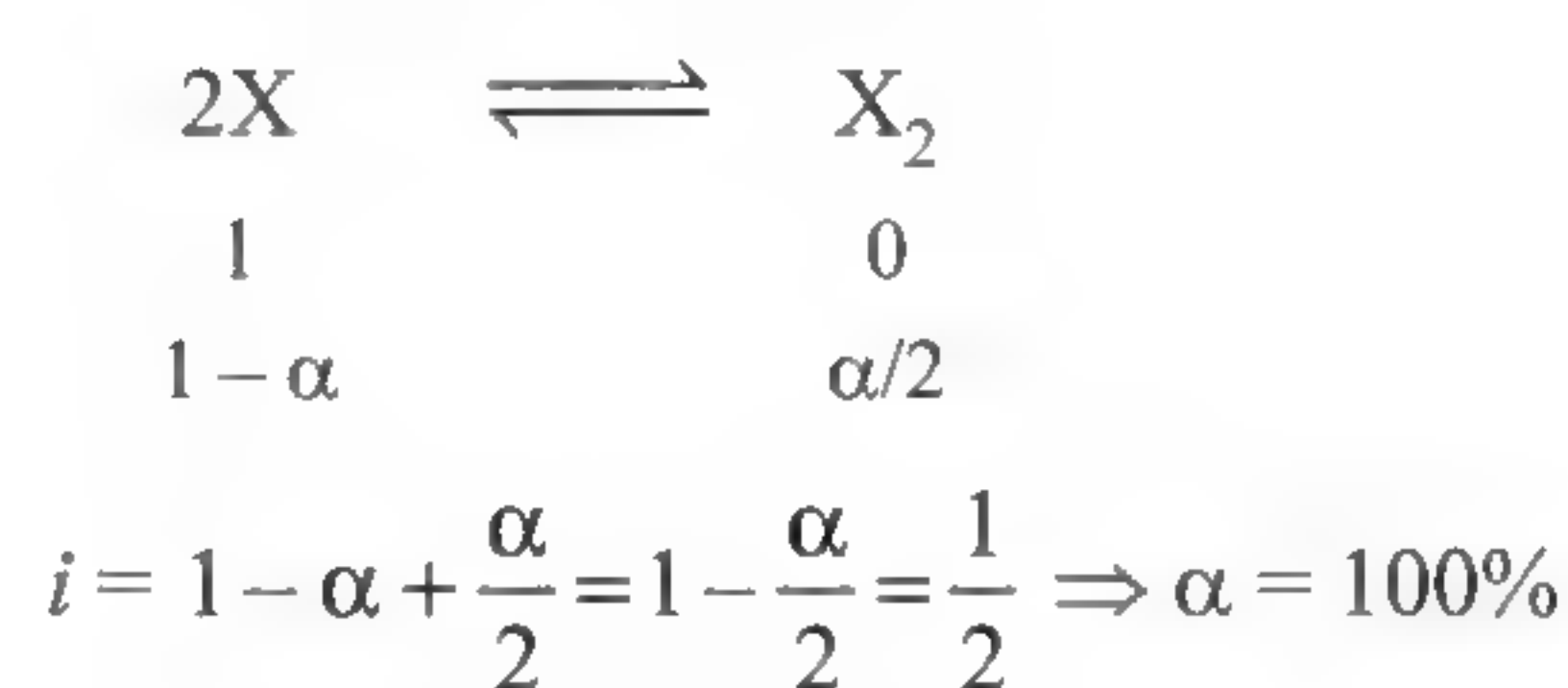
\Rightarrow 0.05 moles of HgI₂ are required for its complex reaction with KI.

Thus, as HgI₂ is being added, the number of solute molecules will decrease causing ΔT_f to decrease \Rightarrow (Causing T_f to increase). When whole of KI has been converted to K₂HgI₄, further addition of HgI₂ does not change T_f since it is a sparingly soluble salt.

$$78. (4) \begin{array}{ccc} \text{KCl} & \text{and} & \text{X} \\ (\text{p moles}) & & (\text{p moles}) \end{array}$$

$$\Delta T_f(\text{KCl}) = iK_f m = 2K_f m$$

$$\Delta T_f(\text{X}) = iK_f m = \frac{1}{4}(2K_f m) \Rightarrow i = \frac{1}{2} (< 1)$$



$$79. (1) \text{ Boiling point is higher if } \Delta T_b \text{ is higher which in turn depends on } m_{\text{eff}} (= im_{\text{eff}})$$

$$0.001 \text{ m urea} < 0.001 \text{ m CH}_3\text{COOH} < 0.001 \text{ M NaCl} < 0.001 \text{ m MgCl}_2$$

$$\text{II} < \text{IV} < \text{I} < \text{III}$$

$$80. (1) \text{ Freezing point is higher if } \Delta T_f \text{ is lower (depends on } m_{\text{eff}}).$$

$$\Rightarrow 0.1 \text{ M Ba}_3(\text{PO}_4)_2 < 0.1 \text{ M Na}_2\text{SO}_4 < 0.1 \text{ M Ethanol}$$

$$\text{II} < \text{III} < \text{I}$$

$$81. (3) \text{ Osmotic pressure is higher if } C_{\text{eff}} \text{ is higher.}$$

$$0.1 \text{ M Glucose} < 1\% \text{ urea } (\approx 0.167 \text{ M}) < 0.1 \text{ M NaCl}$$

$$\text{I} < \text{II} < \text{III}$$

82. (4) NaNO_3 : $i = 2$; $\text{K}_3[\text{Fe}(\text{CN})_6]$: $i = 4$;
 CH_3COOH (weak acid): $i = 2$;
 BaCl_2 : $i = 3$, $\text{C}_6\text{H}_{12}\text{O}_6$: $i = 1$
 $\text{IV} < \text{V} = \text{I} < \text{II} < \text{III}$
83. (4) Addition of salt lowers the freezing point of water and thus snow melts.
84. (1) This is Raoult's law.
85. (1) $\text{Al}_2(\text{SO}_4)_3$ furnishes maximum number of ions.
86. (1) The movement of solvent particles from dilute solution to concentrated one through a semi-permeable membrane is called osmosis.
87. (1) Osmosis occurs from dilute solution to concentrated solution, i.e., exosmosis.
88. (3) Osmotic pressure \propto moles;
 $(\text{NH}_4)_3\text{PO}_4$ furnishes 4 ions in solution.
89. (4) $\text{Fe}_2(\text{SO}_4)_3$ furnishes more number of ions.
90. (4) Addition of a solute increases the boiling point of solution.
91. (3) The scaling of zero degree centigrade is based on this fact.
92. (2) $\pi V = nRT \Rightarrow \pi = \frac{n}{V}RT \Rightarrow \pi = CRT$
93. (4) Freezing point is lowered on addition of solution in it.
94. (2) Perfectly semi-permeable membrane allows the passage of solvent particles only.
95. (1) $\pi \propto \frac{1}{V}$ and not $\pi \propto V$.
96. (1) It is $\text{Cu}_2\text{Fe}(\text{CN})_6$ molecule in gelatinous state to work as semi-permeable in nature.
97. (1) K_f for camphor is maximum (about 40 K m^{-1}).
98. (2) $\pi V = nRT \Rightarrow \pi = \frac{n}{V}RT \Rightarrow \pi = CRT$
99. (2) Elevation in boiling point, osmotic pressure, depression in vapour pressure, and depression in freezing point are colligative properties.
 Colligative properties are properties of solution which depend on the number of particles present in solution.
100. (1) Normal saline is 0.16 M NaCl solution.
101. (1) A solution of M/2 NaCl is isotonic with M glucose. The required condition is $\pi_1 = \pi_2$.
102. (2) AlCl_3 furnishes more ions than CaCl_2 and thus shows higher boiling point.
103. (3) KNO_3 is 100% ionized while CH_3COOH is a weak electrolyte.
104. (3) Colligative properties are properties of solution which depend on the number of particles present in solution and

$$\Delta T_b = \frac{1000 \times K_b' \times n}{W}$$
105. (4) Colligative properties are properties of solution which depends on the number of particles present in solution. $\pi \propto n$.
106. (1) Colligative properties are properties of solution which depend on the number of particles present in solution.
107. (2) It is the definition of osmosis.
108. (4) First three methods involve use of $\text{Cu}_2\text{Fe}(\text{CN})_6$ as semi-permeable membrane which will be dissolved in non-aqueous solvent and thus only Townsend's method having semi-permeable membrane of powdered glass and clay can be used to determine the osmotic pressure of non-aqueous solutions.
109. (3) $\pi \propto n$
110. (3) Van't Hoff factor

$$= \frac{\text{Experimental CP}}{\text{Calculated CP}} = 1 - \alpha + x\alpha + y\alpha$$
 ; For KCl it is 2 and for sugar it is 1.
111. (3) $\frac{\Delta T_{fA}}{\Delta T_{fB}} = \frac{2}{1} = \frac{1}{1/2}$, i.e., B should associate to show higher ΔT .
112. (1) Lowering is always positive.
113. (1) K_b is characteristic constant for given solvent.
114. (1) Normal molecular weight of electrolyte > Experimental molecular weight.
115. (2) NaCl furnishes two ions on complete dissociation.
116. (1) Osmosis will not take place.
117. (4) $\Delta T_f = K_f \times \text{Molarity}$
118. (1) Minimum freezing point means more number of ions
 (1) $0.01 \times 2 = 0.02$
 (2) $0.005 \times 1 = 0.005$
 (3) $0.005 \times 3 = 0.015$
 (4) $0.005 \times 2 = 0.01$
119. (3) More is ΔT_b , more is boiling point.
120. (3) More is ΔT_f , lesser is freezing point
121. (1) Calculation same as in Q. 120.
122. (4) More is ΔT_f , lesser is freezing point.
123. (3) $\pi V = nRT$; $\pi \times \frac{100}{1000} = \frac{5}{342} \times 0.0821 \times 423$
 $\therefore \pi = 5.078 \text{ atm}$
124. (3) $\Delta T_f = 1.86 \times 0.05 = 0.093$;
 $\therefore T_f = 0 - 0.093 = -0.093^\circ\text{C}$
125. (2) $\Delta T_f = 1.86 \times 1 \times 2 = 3.72$;
 $\therefore T_f = 0 - 3.72 = -3.72^\circ\text{C}$;
 NaCl dissociates to give experimental molality
 $= 1 \times 2 = 2$.
126. (1) $\Delta T_f = \frac{1000 \times K_f \times W}{M_w}$
 $= \frac{1000 \times 1.86 \times 342}{100 \times 342} = 1.86$
 $\therefore T_f = 0 - 1.86 = -1.86^\circ\text{C}$
127. (1) $\pi V = nRT$;
 $\therefore \pi \times 1 = 0.1 \times 0.082 \times 273$
128. (4) $\pi = \frac{\pi_1 + \pi_2}{2}$, if equal volumes are mixed, volume of solution becomes double.
129. (3) $\pi \times \frac{63}{1000} = \frac{3}{180} \times 0.0821 \times 288$
 $\therefore \pi = 6.25 \text{ atm}$
 $\therefore V_{\text{solution}} = \text{Weight of solution} \times \text{Density}$
 $= (60 + 3) \times 1 = 63 \text{ mL}$
130. (1) $\Delta T_f = \frac{1000 \times 1.86 \times 17}{46 \times 1000} = 0.69^\circ\text{C}$
 $T_f = 0 - 0.69 = -0.69^\circ\text{C}$

131. (1) For two non-electrolyte solutions, if isotonic $C_1 = C_2$.

$$\therefore \frac{8.6}{60 \times 1} = \frac{5 \times 1000}{Mw_2 \times 100} \Rightarrow Mw_2 = 348.9$$

132. (2) $\pi V_2 = \frac{W_2}{Mw_2} RT$

$$\frac{500}{76} \times \frac{100}{1000} = \frac{4}{Mw_2} \times 0.0821 \times 300$$

$$\therefore Mw_2 = 149.6$$

133. (2) $\Delta T_b = K_b \times m = 0.52 \times 1 \times 2 = 1.04$;

$$\therefore T_b = 100 + 1.04 = 101.04^\circ\text{C}$$

134. (2) For two non-electrolytic solutions, if isotonic, $C_1 = C_2$.

$$\therefore \frac{6.84 \times 100}{342 \times 100} = \frac{1.52 \times 1000}{Mw_2 \times 100} \Rightarrow Mw_2 = 760$$

135. (4) $\pi = CRT \Rightarrow 2.5 = C \times 0.0821 \times 297$

$$\therefore C = 0.1025 \text{ mol L}^{-1}$$



$$\begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 2 \end{array}$$

$$i = \frac{\text{Moles after dissociation}}{\text{Moles before dissociation}} = \frac{3}{1}$$

137. (4) $\frac{P^\circ - P_s}{P^\circ} = \text{Molality} \times (1 - \alpha + x\alpha + y\alpha)$

The value of $P^\circ - P_s$ is maximum for BaCl_2 .

138. (3) $\Delta T_b = K_b \times \text{Molality} \times (1 - \alpha + x\alpha + y\alpha)$.

ΔT_b is more for BaCl_2 as it gives more number of ions, $(1 - \alpha + x\alpha + y\alpha)$ is more for BaCl_2 (it is 3).

139. (4) $\Delta T_b = K_b \times \text{Molality}$

$$\Delta T_f = K_f \times \text{Molality}$$

$$\therefore \frac{\Delta T_b}{\Delta T_f} = \frac{K_b}{K_f} \Rightarrow \Delta T_b = \frac{\Delta T_f \times K_b}{K_f} = \frac{0.186 \times 0.512}{1.86} = 0.0512$$

140. (3) $\Delta T_f = K_f \times \text{Molality} = 1.86 \times 0.05 = 0.093$

$$\text{Thus, freezing point} = 0 - 0.093 = -0.093$$

141. (1) $\Delta T_f = \frac{1000 K_f \times W_2}{Mw_2 \times W_1}$, $[\Delta T = 273 - 271.9 = 1.1]$

$$1.1 = \frac{1000 \times 1.86 \times 1.25}{Mw_2 \times 20}$$

$$Mw_2 = 105.68$$

142. (2) For non-electrolytic solutions, if isotonic, $C_1 = C_2$

$$= \frac{5 \times 1000}{342 \times 100} = \frac{1 \times 1000}{Mw_2 \times 100}$$

$$\therefore Mw_2 = 68.4$$

143. (1) $\pi = \frac{n}{V} RT$

$$n = \frac{\pi V}{RT} = \frac{7.40 \times 1}{0.0821 \times 300} = 0.3$$

144. (3) $\Delta T_f = \text{Molality} \times K_f \times i$

$$3.72 = 1 \times 1.86 \times i$$

$i = 2$, hence complex is binary.

Also, C.N of Pt is 6 and complex is hydrated.



145. (4) Larger the value of (i) , Smaller the freezing point (d) is a case of non-electrolytes, $i = 1$.

146. (2) $\Delta T_f = K_f \times m' \times i$

$$\frac{\Delta T(\text{urea})}{\Delta T(\text{CH}_3\text{COOH})} = \frac{m'(\text{urea})}{m'(\text{CH}_3\text{COOH}) \times i}$$

$$i = 1.1 \quad (i = 1 \text{ for urea})$$

$$= (1 + x) \text{ for } \text{CH}_3\text{COOH}$$

$$x = 0.1$$

$$\therefore [\text{H}^\oplus] = Cx = 0.001$$

$$\therefore \text{pH} = 3$$

147. (1) $\text{pH} = 2$

$$[\text{H}^\oplus] = 0.01 \text{ M} = Cx = 0.1x$$

$$x = 0.1$$

$$i = 1 + x = 1.1$$

$$\pi = i \frac{n}{V} RT = iMRT = 1.1 \times 0.1RT = 0.11RT$$

148. (1) $\frac{\Delta P}{P^\circ} = \frac{W_2 \times Mw_1}{Mw_2 \times W_1}$

$$\Delta P = \frac{1 \times 18}{1000} \times 760 = 13.68$$

(at 100°C , VP = 760 torr)

149. (4) $\pi = MRT$

i. $\pi = RT$

ii. $\pi = RT$

iii. $\pi = RT$ (mix has concentration = 1 M)

150. (4) Osmosis of water and not of ion takes place.

151. (2) m (benzoic acid)

$$= \frac{1000 K_b W_1}{\Delta T_b W_2} = 244 \text{ (twice of actual molecular weight)}$$

152. (2) $25 \times M_{(\text{KCl})} = 20 \times 1 M_{(\text{AgNO}_3)}$

$$\therefore M_{(\text{KCl})} = 0.8$$

$$\Delta T_f = M' K_f i$$

$$= 0.8 \times 2 \times 2 = 3.2^\circ$$

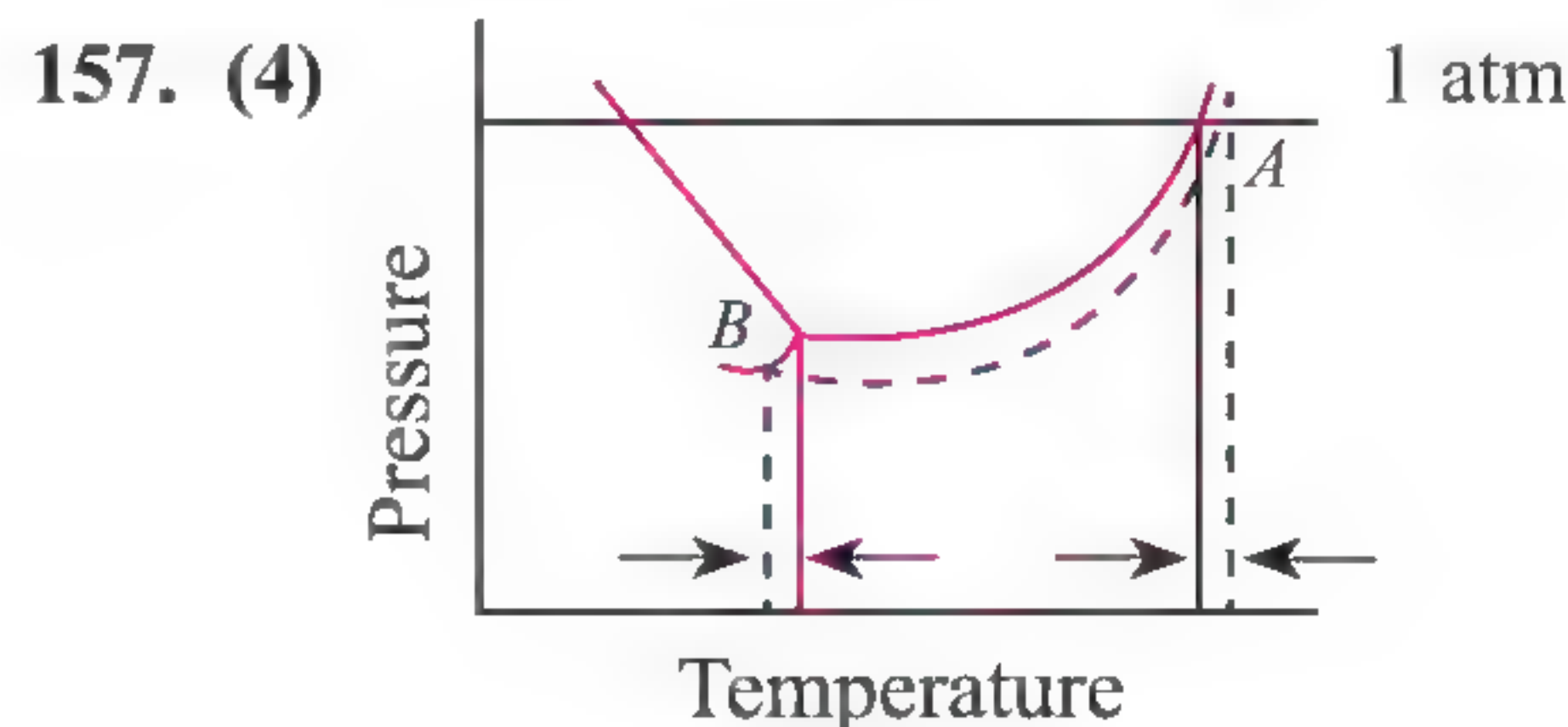
153. (3) 154. (1) 155. (4)

156. (1) $\therefore \Delta T = \frac{1000 \times K_f' \times w_2}{Mw_2 \times m}$

$$93 = \frac{1000 \times 1.86 \times 50}{62 \times W} \quad (Mw_2 = 62 \text{ g})$$

$$\therefore W = 161.29$$

$$\therefore \text{Ice separated} = 200 - 161.29 = 38.71 \text{ g}$$



Point A represents the elevation of boiling point and point B represent the depression in freezing point.

$$\left. \begin{array}{l} A = \Delta T_b \\ B = \Delta T_f \end{array} \right\}$$

158. (1) Elevation in boiling point \propto concentration of a solution. thus, the order of concentration of solutions is I < II < III.

159. (1) $\pi = CRT$

$$\pi \propto T [C = \text{const.}]$$

160. (4) Only solvent molecules can pass through SPM so only dilution is possible.

161. (4) $\pi_{\text{NaCl}} = \pi_x$

For NaCl, $i = 2$

$$(i)_{\text{NaCl}} \times C_1 RT = (i)_x C_2 RT$$

$$2 \times 0.3 = (i)_x \times 0.2$$

$$(i)_x = 3.0$$

162. (1) Mass of oxygen = $\frac{20}{100} \times 0.04 = 0.008 \text{ g/L}$

$$\text{Mass of nitrogen} = \frac{80}{100} \times 0.02 = 0.016 \text{ g/L}$$

163. (2) $\therefore n_{\text{O}_3}$ dissolved in 100 g water at 1.0 atm

$$= \frac{40 \times 1 \times 10^{-3}}{0.0821 \times 300}$$

$\therefore n_{\text{O}_3}$ dissolved in 400 g water at 4 atm

$$= \frac{4 \times 4 \times 40 \times 10^{-3}}{24.63} = \frac{640 \times 10^{-3}}{24.63}$$

$$\therefore W_{\text{O}_3} = \frac{640 \times 10^{-3}}{24.63} \times 48 \approx 1.2 \text{ g (Mw of O}_3 = 48 \text{ g)}$$

164. (4) As Temperature increases K_H increases

165. (2) $W_{\text{Gas}} \propto P_{\text{Gas}}$ at constant T .

166. (1) $P_{\text{N}_2} = (K_H)_{\text{N}_2} X_{\text{Gas}}$

$$1 = (K_H)_{\text{N}_2} \times \left(\frac{0.02/28}{\frac{0.02}{28} + \frac{1000}{18}} \right)$$

$$(K_H)_{\text{N}_2} = 7.7 \times 10^4 \text{ atm}$$

167. (2) C.N. of $\text{Co}^{+3} = 6$

Compound (X) is represented as:



$$\Delta T_f = i K_f m = 2 \times 1.86 \times \frac{23.35 \times 1000}{233.5 \times 1000} = 0.372$$

$$T_f = 0 - 0.372 = -0.372^\circ\text{C}$$

168. (1) Correct statement (1)

Partial pressure of a gas is related to mole fraction of the dissolved gas and K_H

$$\therefore P = x_2 K_H.$$

169. (1) I. $\text{Hg}_2\text{Cl}_2 \rightleftharpoons \text{Hg}_2^{2+} + 2\text{Cl}^-$ (3 ions)

$$i = (\text{Number of ions} \times \alpha) + (1 - \alpha)$$

$$= (3 \times 0.6) + 0.4 = 2.2$$

II. $12 \text{ B} \rightleftharpoons \text{B}_{12}$ (Boron exists as icosahedron structure)

$$i = (\text{Number of ions} \times \alpha) + (1 - \alpha)$$

$$= \left(\frac{1}{12} \times 0.6 \right) + (1 - 0.6)$$

$$= \frac{1}{20} + 0.4 = 0.05 + 0.4 = 0.45$$

170. (1) $\Delta T_b = K_b \times m$

$$\Delta T_f = K_f \times m$$

$$\frac{\Delta T_f}{\Delta T_b} \frac{K_f}{K_b} = \frac{RT_f^f}{RT_b^2} \frac{1000 l_v}{1000 l_f} = \frac{T_f^2 l_v}{T_b^2 l_f}$$

$$T_b = 100 + 273 = 373 \text{ K}$$

$$T_f = 273 \text{ K}$$

$$\Delta T_b = 100.3 - 100 = 0.3^\circ\text{C.}$$

$$\frac{\Delta T_f}{0.3} = \frac{(272)^2}{(373)^2} \times \frac{500}{100}$$

$$\Delta T_f = \frac{(273)^2 \times 1.5}{(373)^2}$$

Multiple Correct Answers Type

1. (1, 2)

$$P_M = P_A^\circ \cdot \chi_A + P_B^\circ \cdot \chi_B; \text{ Also, } P' = P_M \cdot \chi_{A(V)} = P_A^\circ \cdot \chi_{A(l)}$$

$$= P_A^\circ \cdot \chi_A + P_B^\circ \cdot (1 - \chi_A)$$

$$\therefore \chi_A = \frac{P_M - P_B^\circ}{P_A^\circ - P_B^\circ}$$

2. (1, 2, 4)

For immiscible liquids

$$P_A' = P_M \cdot \chi_A'; \quad P_B' = P_M \cdot \chi_B'$$

$$\therefore \frac{P_A'}{P_B'} = \frac{\chi_A'}{\chi_B'} = \frac{n_A}{n_B} = \frac{W_A \times M_{wB}}{M_{wA} \times W_B}$$

If $P_A' > P_B'$, then $n_A > n_B$.

3. (1, 3, 4)

$$\frac{\Delta P}{P^\circ} = \frac{n_2}{n_1} = \frac{n_2 \times M_{w1} \times 1000}{W_1 \times 1000} = \frac{\text{Molality} \times M_{w1}}{1000}$$

$$\text{For electrolyte } \frac{\Delta P}{P^\circ} = \frac{\text{Molality} \times M}{1000} \times (1 + 3\alpha)$$

($M_{w1} = 18$ for H_2O)

$$\text{Also, } \pi_{\text{obs}} = C \times R \times T (1 + 3\alpha)$$

$$\therefore \frac{\Delta P}{P^\circ} = \frac{\pi_{\text{obs}}}{RT} \times \frac{18}{1000}$$

$$\Delta T_{f \text{ obs}} = K_f \times \text{molality} \times (1 + 3\alpha)$$

$$\frac{\Delta P}{P^\circ} = \frac{\Delta T_{f \text{ obs}} \times 18}{K_f \times 100}$$

$$i = (1 + 3\alpha) = \frac{\text{Calculated molecular weight}}{\text{Observed molecular weight}}$$

Therefore, molecular weight of $\text{K}_3\text{PO}_4 = M_{\text{obs}} \times (1 + 3\alpha)$

4. (1, 2, 3, 4)

5. (1, 3)

6. (1, 2)

Benzene and toluene \Rightarrow Ideal solution.

$$P_{\text{Total}} = P_A^\circ \chi_A + P_B^\circ \chi_B = 42 \times \frac{1}{3} + 36 \times \frac{2}{3} = 38 \text{ mm Hg}$$

$$\chi_{\text{Benzene}}^V = \frac{P_{\text{Benzene}}}{P_{\text{Total}}} = \frac{42 \times \frac{1}{3}}{38} = \frac{7}{19}$$

7. (2, 4)

 $\Delta_{\text{mixing}}V = 0; \Delta_{\text{mixing}}H = 0 \Rightarrow$ for ideal solutions.

8. (1, 2)

9. (2, 4)

10. (1, 3)

On addition of non-volatile substance, according to the colligative property, the vapour pressure of solution decreases and its boiling point increases.

11. (1, 4)

12. (1, 2, 3)

13. (3)

14. (1, 3, 4)

Greater is the intermolecular force on mixing, more negative will be the deviation $p < P_A^\circ \chi_A + P_B^\circ \chi_B$.

Experimental vapour pressure will be less than calculated vapour pressure.

15. (1, 4)

Depending on the vapour pressures of the pure components 1 and 2, total vapour pressure over the solution decreases or increases with the increase of the mole fraction of component 1.

16. (1, 2, 3)

Boiling point of $\text{CCl}_4 <$ that of SiCl_4 . the vapour must always be richer in more volatile component. Hence, the upper curve represents the composition of the vapour and the lower curve represents the composition of the solution at the corresponding boiling point.

17. (1, 2, 4)

Benzene and toluene mix to form an ideal solution.

18. (2, 3)

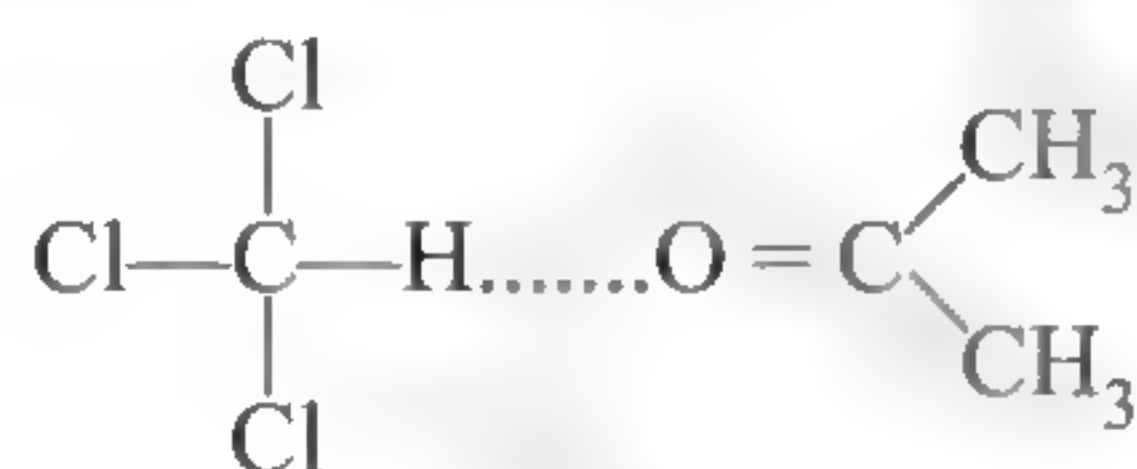
Azeotrope is a type of liquid mixture, having a definite composition, and boiling like a pure liquid.

19. (2, 3, 4)

For a reaction to take place ΔG must be negative.

20. (1, 2, 4)

When CHCl_3 and $(\text{CH}_3)_2\text{CO}$ are mixed, the hydrogen bonding takes place between the two molecular species due to which the escaping tendency of either of the liquid molecules become less. Consequently, the boiling point of solution increases.



21. (1, 2)

$$\pi = CRT \Rightarrow \pi = \frac{n_2 RT}{V} = \frac{W_2 RT}{Mw_2 V}$$

22. (2, 4)



$$i = 3$$

23. (2, 3)

Adding K_2SO_4 into BaCl_2 solution will result into precipitation of BaSO_4 which is non-volatile, and therefore boiling point of solution will be increased and its freezing point will decrease.

24. (1, 2, 3)

Refer Section 2.10.4.

25. (1, 3, 4)

(1) There will be a depression in the freezing point by the addition of glucose in water.

(2) α increases as concentration decreases.

$$(3) \Delta_{\text{sol}}H = \underset{(-ve)}{\Delta_{\text{latice}}H} + \underset{(-ve)}{\Delta_{\text{hyd}}H}$$

(4) Mixing of solution is always accompanied by an increase in entropy (randomness).

26. (1, 4)

$$\text{NaCl: } 0.5 \text{ M } (i = 2) \Rightarrow C_{\text{eff}} = 0.5 \times 2 = 1 \text{ M}$$

$$\text{C}_6\text{H}_5\text{COOH: } 2.0 \text{ M } \left(i = \frac{1}{2} \right) \Rightarrow C_{\text{eff}} = 2 \times \frac{1}{2} = 1 \text{ M}$$

(1) $\pi = C_{\text{eff}} RT \Rightarrow \pi$ is same as C_{eff} is same.

(2) Since both the solutions have different solvents, vapour pressure will be different.

(3) Solutions are isotonic.

(4) $\Delta T_f = iK_f m \Rightarrow \Delta T_f$ for solution II will be more as $(K_f)_{\text{benzene}} > (K_f)_{\text{water}}$.

27. (2, 3, 4)

28. (3, 4)

Osmotic pressure is a colligative property, therefore, it depends upon the number of constituents of solution. It also depends upon temperature as $\pi = CRT$.

29. (1, 2, 3, 4)

$$\text{Molarity} = \frac{1.2575 \times 1000}{251.5 \times 250} = 0.02 \text{ M, } \pi = CRT$$

$$\therefore \pi_{\text{obs}} = 0.02 \times 0.0821 \times 300 = 0.4926 \text{ atm} \\ = 374.38 \text{ mm}$$

$$\frac{\pi_{\text{obs}}}{\pi_{\text{cal}}} = i = \frac{1.478 \times 760}{374.38} = 3$$

$$\therefore \alpha = \frac{i-1}{n-1} \text{ and } \alpha = 1,$$

$$\therefore n = 3$$

Also,



	0.02	0	0	0
Eq conc	0	0.02	0.02	0.02

30. (1, 3, 4)

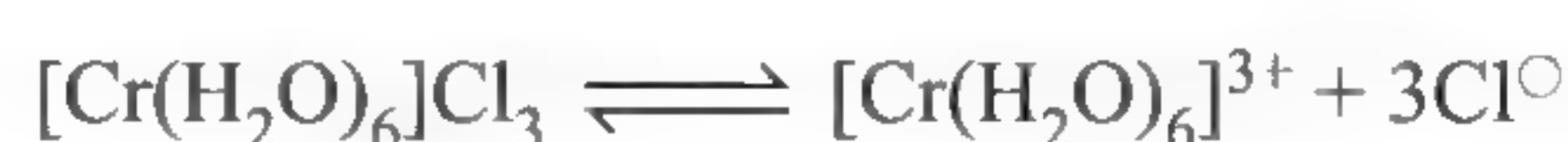


$$\pi = CRT(1 - \alpha + x\alpha + y\alpha)$$

$$98.52 = 1 \times 0.0821 \times 300 \times (x + y) (\alpha = 1)$$

$$\therefore (x + y) = 4$$

$\therefore \text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ can be written as



1	0	0
$1 - \alpha$	α	3α

3 mol of AgNO_3 will react with 1 mol of $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$.



moles $2 \times 1 = 2$	$1 \times 6 = 6$	0	0
0	0	2	6

\therefore Moles of AgCl formed = 6

Weight of AgCl formed = $6 \times 143.5 = 861$ g

$$[\text{Cr}(\text{H}_2\text{O})_6](\text{NO}_3)_3 = \frac{2}{3}$$

$$\pi = CRT \times (1 + 3\alpha) = \frac{2}{3} \times 0.0821 \times 300 \times 4 = 65.68 \text{ atm}$$

31. (2, 3)

32. (2, 3)

Vapour pressure of solution containing non-volatile solute is always smaller than that of solvent. Points, a and b represent the boiling points of solvent and solution respectively (temperatures at which their V.P. = 1 atm each). Hence gas ab = $K_b m$ = elevation of boiling point.

33. (1, 2, 3)

$$\pi = CRT$$

Comparing with $y = mx + c$

Slope RT

Linked Comprehension Type

Paragraph 1

1. (3) Hypertonic solutions have higher osmotic pressure and therefore they have higher concentration. When a plant cell is kept in hypertonic solution, water from plant cell moves to hypertonic solution and therefore the plant cell gets shrunked.

2. (3)

3. (3) The osmotic pressure should be same for glucose solution and bloodstream otherwise veins would get shrunked.

4. (2, 5)

Isotonic solutions have same osmotic pressure as well as same concentration, i.e., molarity.

$$\pi \propto C$$

5. (1, 2)

$$\pi = CRT$$

Paragraph 2

6. (2) Isotonic solution have same molarity.

$$\text{Molarity of 18 g glucose} = \frac{18}{276} \times \frac{1000}{1000} = 0.065$$

$$\text{Molarity of 34.2 g sucrose} = \frac{34.2}{518} \times \frac{1000}{1000} = 0.066$$

The concentration of 18 g L^{-1} glucose is same to 34.2 g L^{-1} sucrose.

7. (1) For solutions 1 and 2 the concentration in compartment B is higher than in A.

8. (1)

9. (2) In hypertonic solution osmotic pressure is higher, therefore, volume rise is higher in B.

10. (4) Isotonic solutions have same concentration and therefore same rise in osmotic pressure.

Paragraph 3

11. (3) $\chi_{\text{Ethanol}} = 0.9;$ $\chi_{\text{water}} = 0.1$
(Solvent \equiv A) (Solute \equiv B)

$$\begin{aligned} \Delta T_f &= K_f \cdot m = K_f \cdot \frac{\chi_B}{1 - \chi_B} \times \frac{1000}{Mw_A} \\ &= 2 \times \frac{0.1}{0.9} \times \frac{1000}{46} = 4.83 \text{ K} \end{aligned}$$

$$T_f = T_f^\circ - \Delta T_f = 155.7 - 4.83 = 150.87 \text{ K}$$

12. (2) $P_{\text{Total}} = P_A^\circ \chi_A$ [\because Solute is to be taken as non-volatile]
 $= 40 \times 0.9 = 36 \text{ mm Hg}$

13. (2) $\chi_{\text{ethanol}} = 0.1;$ $\chi_{\text{water}} = 0.9$
(Solvent \equiv B) (Solute \equiv A)

$$\begin{aligned} \Delta T_b &= K_b \cdot m = K_b \cdot \frac{\chi_B}{1 - \chi_B} \times \frac{1000}{Mw_A} \\ &= 0.52 \times \frac{0.1}{0.9} \times \frac{1000}{18} = 3.2 \text{ K} \end{aligned}$$

$$T_b = T_b^\circ + \Delta T_b = 373 + 3.2 = 376.2 \text{ K}$$

Paragraph 4

14. (1) Pressure of N_2 in X = 1.9 atm

Total pressure of vessel X = 2 atm

$$\therefore \text{Pressure of } \text{H}_2\text{O(g)} \text{ in X at 300 K} = 2 - 1.9 = 0.1 \text{ atm}$$

15. (2) Pressure of N_2 in Y = 3.8 atm

$$\text{Pressure of } \text{N}_2 \text{ at 320 K} = \frac{3.8}{300} \times 320 = 4.05 \text{ atm}$$

16. (1) Total pressure at 320 K = 4.32 atm

$$\therefore \text{Pressure of water vapour at 320 K} = 4.32 - 4.05 = 0.27 \text{ atm}$$

17. (4) Enthalpy of vapourization ($\Delta_{\text{vap}}H$)

$$\Rightarrow \log \frac{p_1}{p_2} = \frac{\Delta H}{2.303R} \left[\frac{1}{300} - \frac{1}{320} \right]$$

$$\Rightarrow \log \frac{0.27}{0.10} = \frac{\Delta H}{2.303R} \left[\frac{1}{300} - \frac{1}{320} \right]$$

$$= \Delta_{\text{vap}}H = 39.65 \text{ kJ mol}^{-1}$$

Paragraph 5

18. (1) The composition of 50% H_2O and 50% HNO_3 will lie in between the azeotropic mixture and pure H_2O . Therefore, distillation of such composition will give pure H_2O and azeotropic mixture.

19. (3) The composition of 80% HNO_3 and 20% H_2O lies in between the azeotropic mixture and pure HNO_3 . Therefore, distillation of it gives pure HNO_3 and azeotropic mixture.

20. (4)

21. (3) In Fig 2.25(a), A and B do not form any azeotropic mixture, therefore they can be easily separable.

22. (1, 3, 4)

Composition Q lies closer to component B, and at temperature T_1 , vapour phase will contain more of B.

Matrix Match Type

1. (a \rightarrow p, r) $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$ = Azeotropic mixture (at a particular composition) shows positive deviation.
(b \rightarrow q, t) $\text{C}_2\text{H}_5\text{Br} + \text{C}_2\text{H}_5\text{I}$ = Ideal solution; obeys Raoult's law.
(c \rightarrow q, t) $p_A = P_A^\circ \chi_A$ = Ideal solution (with non-volatile solute)
(d \rightarrow p, s) $\text{H}_2\text{O} + \text{H}_2\text{SO}_4$ = Azeotropic mixture (at a particular composition) shows negative deviation.

2. (a \rightarrow p; b \rightarrow q; c \rightarrow r)

3. Osmotic pressure (π) = $iCRT$; i = Van't Hoff factor

(a \rightarrow r) i is same for glucose, urea, fructose i.e., $i = 1$

(b \rightarrow s) NaCl ; $i = 2$; K_2SO_4 ; $i = 3$;
 MgCl_2 ; $i = 3$

- (c → p) $\text{Al}_2(\text{SO}_4)_3$; $i = 5$; Na_3PO_4 ; $i = 4$;
 $\text{K}_4[\text{Fe}(\text{CN})_6]$; $i = 5$
- (d → q) Glucose; $i = 1$; NaCl ; $i = 2$
 CaCl_2 ; $i = 3$
4. (a → p) Hypertonic solutions have higher osmotic pressure than some other solutions.
 (b → q) Isotonic solutions have same osmotic pressure than some other solutions.
 (c → r)
 (d → s)
5. (a → q) Lowering of vapour pressure = $P^\circ - P_s$.
 = Pressure of pure solvent – Pressure of solution
 (b → s)
 (c → r)
 (d → p)
6. a—ii—p; b—i—q; c—iv—r; d—v—t; e—iii—s
 Refer to section 2.2 page 2.4 Physical Chemistry Part-2
7. a—ii, iv—q, r; b—i, iv—p, s; c—iii—q; d—v—t
 Refer to section 2.4 page 2.11 Physical Chemistry Part-2

Numerical Value Type

1. (1) $\Delta T_b = iK_b m$
 $0.27 = i \times 0.54 \times \frac{12.2}{122} \times \frac{1000}{100}$
 or $i = 0.5$
 Therefore, benzene associated as dimer, i.e., 2.
2. (2) For urea, $i = 1$, while for BaCl_2 , $i = 3$, therefore, the ratios of any colligative property for BaCl_2 solution to urea solution is 3.
3. (4) $i = 1$, for non-electrolyte
4. (2) $\Delta T = iK_f m$
 $(273 - 269.28) = i \times 1.86 \times 1$
 $3.72 = i \times 1.86$
 $i = 2$
 $\alpha = \frac{i-1}{n-1}$; ($\alpha = 100\% = 1$)
 $1 = \frac{2-1}{n-1} \Rightarrow n = 2$
5. (4) Total colligative properties are four.
6. (4) $\Delta T_b = iK_b m$
 For NaCl solution, $i = 2$
 \therefore for NaCl , $\Delta T_b = 2$
7. (4) Let $\pi_1 = 200$ mm; $T_1 = 283$
 $\pi_1 = 105.3$; $T_2 = 298$
 Now, $\pi = \frac{n}{V} RT$
 At T_1 , $200 = \frac{n}{V_1} R \times 283$... (i)
 At T_2 , $50 = \frac{n}{V_2} \times R \times 298$... (ii)

Dividing Eq. (i) by Eq. (ii), we get

$$\frac{200}{105.3} = \frac{V_2}{V_1} \times \frac{283}{298} \Rightarrow V_2 = 2V_1$$

$$8. (2) \pi = CRT = \frac{\left(\frac{W_2}{Mw_2}\right)RT}{V}$$

Given $W_2 = 40$ g

$Mw_2 = 246$

$T = 27^\circ\text{C} = 300$ K

$V = 1$ L

Substituting all the values, we get

$$\pi = \frac{40}{246} \times 0.082 \times 300 = 4 \text{ atm}$$

Archives

JEE Advanced

Single Correct Answer Type

1. (1) $P_{\text{N}_2} = 5 \times 0.8 = 4$
 Applying Henry's law, we get
 $P_{\text{N}_2} = K_H \times \chi_{\text{N}_2}$
 or $4 = 10^5 \times \chi_{\text{N}_2}$
 $\chi_{\text{N}_2} = 4 \times 10^{-5}$
 $\frac{n_{\text{nitrogen}}}{n_{\text{nitrogen}} + n_{\text{H}_2\text{O}}} = 4 \times 10^{-5}$
 or $\frac{n_{\text{nitrogen}}}{n_{\text{nitrogen}} + 10} = 4 \times 10^{-5}$
 or $n_{\text{nitrogen}} = 4 \times 10^{-4}$.
2. (1) $\Delta T_f = iK_f m = 4 \times 1.86 \times \frac{0.1}{329} \times \frac{1000}{100}$
 $= 0.0226$
 (For $\text{K}_3[\text{Fe}(\text{CN})_6] \rightleftharpoons 3\text{K}^+ + [\text{Fe}(\text{CN})_6]^{3-}$
 $i = 4$)
3. (1) Therefore, the freezing point is $-2.3 \times 10^{-2}^\circ\text{C}$.
 $\Delta T_b = 2^\circ\text{C}$; $W_2 = 2.5$ g
 $W_1 = 100$ g; $K_b = 0.76$ K. kg mol $^{-1}$
 $p_s = ?$
 $\Delta T_b = K_b \times m$
 $2 = 0.76 \times m \Rightarrow m = \frac{2}{0.76}$
 We know;
 $m = \frac{n_2 \times 1000}{n_1 \times Mw_1}$ (Mw_1 (H_2O) = 18)
 $\frac{n_2}{n_1} = x_2 = \frac{m \times Mw_1}{1000} = \frac{2 \times 18}{0.76 \times 1000}$
 $\therefore \frac{p^\circ - p_s}{p_s} = x_2 = \frac{2 \times 18}{0.76 \times 1000} = \frac{36}{760}$
 $760 - p_s = \frac{36}{760} p_s$
 $\left(\frac{36}{760} p_s + p_s\right) = 760$
 $p_s \left(\frac{36}{760} + 1\right) = 760$
 $1.047 p_s = 760$
 $p_s = \frac{760}{1.047} = 725.6 \text{ torr} \approx 724 \text{ torr}$

$$4. (2) \frac{P^0 - P}{P^0} = X_{\text{value}} = \frac{n_1}{n_1 + n_2}$$

$$\frac{185 - 183}{185} = \frac{2}{185} = \frac{1.2 / M}{\frac{12}{M} + \frac{100}{58}} \Rightarrow M = 64$$

$$5. (4) \Delta T_f = K_f \times m = K_f \times \frac{w_2 \times 1000}{Mw_2 \times w_1}$$

$$= 2 \times \frac{34.5 \times 1000}{46 \times 500} = 2 \times 1.5 = 3$$

Freezing point of ethanol + water mixture
 $= 273 - \Delta T_f = 273 - 3 = 270$

Multiple Correct Answers Type

1. (2, 3, 4)

For ideal solution,

$$\Delta S_{\text{system}} > 0$$

$$\Delta S_{\text{surrounding}} = 0$$

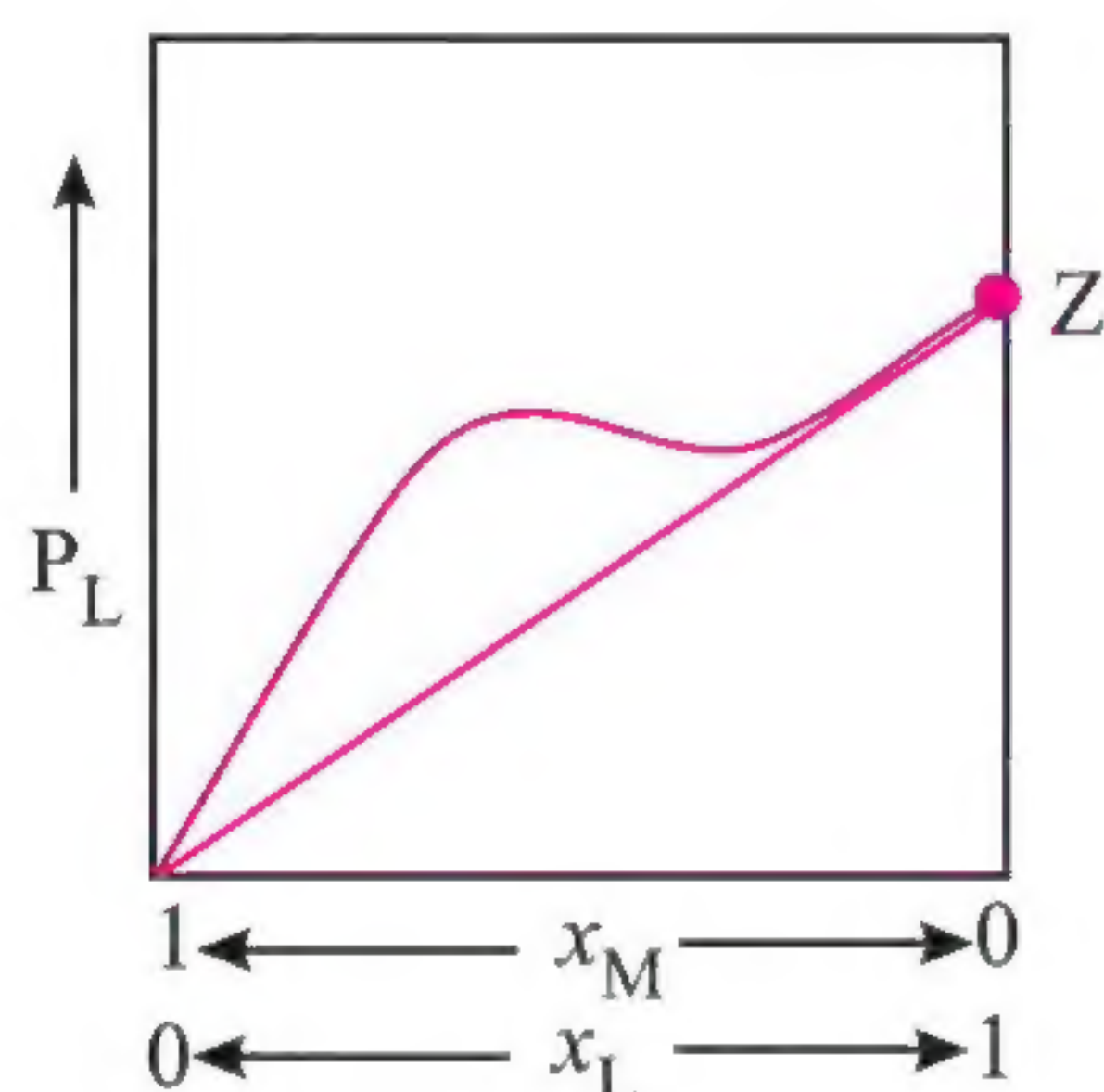
$$\Delta H_{\text{mixing}} = 0$$

2. (1, 2) Factual

Benzene + toluene will form ideal solution.

Phenol + aniline will show negative deviation.

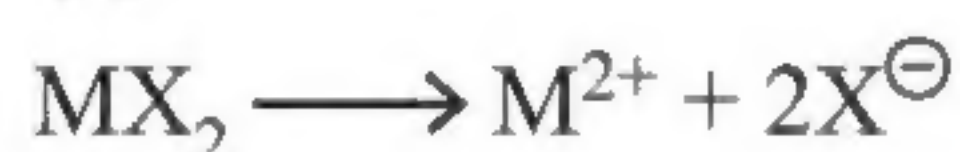
3. (2, 4)



From graph it is clear that there is +ve deviation w.r.t. L. Therefore option A is correct. When $x_L \rightarrow 1$, then Z will have value equal to P_L^0 (vapour pressure of pure L). Therefore option (4) is also correct.

Numerical Value Type

1. (2)



$$1 \quad 0 \quad 0$$

$$1 - \alpha \quad \alpha \quad 2\alpha$$

$$i = 1 - \alpha + \alpha + 2\alpha = 1 + 2\alpha = 1 + 2 \times 0.5 = 2$$

2. (19)

$$x_A = \frac{1}{2}, x_B = \frac{1}{2}$$

$$P_T = P_A^0 \frac{1}{2} + P_B^0 \times \frac{1}{2}$$

$$(\text{Given } P_A^0 = 20)$$

$$90 = 45 \times 2 = P_A^0 + P_B^0 \quad \dots(1)$$

$$P_B^0 = 90 - 20 = 70$$

$$22.5 - P_A^0 x_A + P_B^0 (1 - x_A)$$

$$= 20x_A + 70(1 - x_A)$$

$$22.5 = 20x_A + 70 - 70x_A = 70 - 50x_A$$

$$x_A = \frac{47.5}{50} = \frac{19}{20}$$

$$x_B = \frac{1}{20}$$

$$\frac{x_A}{x_B} = \frac{\frac{19}{20}}{\frac{1}{20}} = 19$$

3. (0.05)

$$2 = 2 \times K_{b(x)} m$$

$$1 = 2 K_{b(y)} m$$

$$\frac{K_{b(x)}}{K_{b(y)}} = 2$$

$$\Delta T_{b(x)} = \left(1 - \frac{\alpha_1}{2}\right) K_{b(x)} m \quad 2S \rightleftharpoons S_2$$

$$1 - \alpha \quad \frac{\alpha}{2}$$

$$\Delta T_{b(y)} = \left(1 - \frac{\alpha_2}{2}\right) K_{b(y)} m \quad i = 1 - \alpha + \frac{\alpha}{2}$$

$$3 = \frac{\Delta T_{b(x)}}{\Delta T_{b(y)}} = \frac{\left(1 - \frac{\alpha_1}{2}\right) K_{b(x)}}{\left(1 - \frac{0.7}{2}\right) K_{b(y)}} \quad i = 1 - \frac{\alpha}{2}$$

$$3 = \frac{\left(1 - \frac{\alpha_1}{2}\right) \times 2}{\left(1 - \frac{0.7}{2}\right)}$$

$$\left(1 - \frac{\alpha_1}{2}\right) = \frac{3 \times 0.65}{2} = 1.5 \times 0.65$$

$$\alpha_1 = 0.05$$

4. (1.02)

$$\frac{p^0 - p_s}{p_s} = i \left(\frac{n_{\text{solute}}}{n_{\text{solvent}}} \right)$$

$$\frac{650 - 640}{640} = 1 \times \frac{0.5 \times 78}{M \times 39}$$

$$\Rightarrow Mw_2 = 64 \text{ g}$$

$$\Delta T_f = K_f \times m = 5.12 \times \frac{0.5 \times 1000}{64 \times 39} \Rightarrow \Delta T_f = 1.02$$

5. (0.20)

$$P_{\text{total}} = p_A^{\circ} x_A + p_B^{\circ} x_B$$

$$0.3 = p_A^{\circ} \times 0.25 + p_B^{\circ} \times 0.75 \quad \dots(i)$$

$$0.4 = p_A^{\circ} \times 0.50 + p_B^{\circ} \times 0.50 \quad \dots(ii)$$

$$\text{On solving, } p_A^{\circ} = 0.6 \text{ bar, } p_B^{\circ} = 0.2 \text{ bar,}$$

6. (100.1)

Initially for solution A[0.1 m AgNO₃]

$$\Delta T_b = i K_b m$$

$$\Delta T_b = 2 \times 0.5 \times 0.1 \quad [\because i \text{ for AgNO}_3 = 2]$$

$$\text{Also, } \Delta T_b = T_b - T_b^{\circ}$$

$$T_b - 100 = 0.1$$

$$T_b = 100.1^{\circ}\text{C}$$

$$\text{i.e., } x = 100.1^{\circ}\text{C}$$



0.1V	0.1 V
ion	millimole
Ag^+	0.1 V
NO_3^-	0.1 V
Ba^{2+}	0.1 V
Cl^-	0.2 V

$$\begin{aligned}\therefore \Delta T_b &= iK_b \times m \\ &= 0.5 \left[\frac{0.1\text{V} + 0.1\text{V} + 0.1\text{V}}{2\text{V}} \right] \\ &= 0.5 \times \frac{0.3}{2} = 0.075\end{aligned}$$

$$T_b - 100 = 0.075$$

$$T_b = 100.075$$

$$\text{Difference in } T_b = 100.1 - 100.075 = 0.025 = 2.5 \times 10^{-2}$$

$$y = 2.5$$